

L1 STRUCTURE UPLOADED

=> d his

(FILE 'HOME' ENTERED AT 21:59:15 ON 28 MAR 2008)

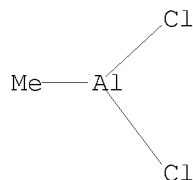
FILE 'REGISTRY' ENTERED AT 22:00:43 ON 28 MAR 2008

L1 STRUCTURE UPLOADED

=> d l1

L1 HAS NO ANSWERS

L1 STR



Structure attributes must be viewed using STN Express query preparation.

=> s l1 full

FULL SEARCH INITIATED 22:01:10 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 6578 TO ITERATE

100.0% PROCESSED 6578 ITERATIONS

158 ANSWERS

SEARCH TIME: 00.00.01

L2 158 SEA SSS FUL L1

=> fil caplus

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

178.36

178.99

FILE 'CAPLUS' ENTERED AT 22:01:19 ON 28 MAR 2008

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=> s 12/prep
      521 L2
      4549398 PREP/RL
L3      90 L2/PREP
      (L2 (L) PREP/RL)

=> s 13 and py<=2003
      23980118 PY<=2003
L4      79 L3 AND PY<=2003

=> s 14 and aluminum metal
      1027344 ALUMINUM
      1819660 METAL
      2219 ALUMINUM METAL
      (ALUMINUM(W)METAL)
L5      0 L4 AND ALUMINUM METAL

=> s 14 and metallic aluminum
      288098 METALLIC
      1027344 ALUMINUM
      704 METALLIC ALUMINUM
      (METALLIC(W)ALUMINUM)
L6      0 L4 AND METALLIC ALUMINUM

=> d 14 1-79 bib abs

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L4  ANSWER 1 OF 79  CAPLUS  COPYRIGHT 2008 ACS on STN
AN  2003:752416  CAPLUS
DN  140:406839
TI  Metallated triphenylphosphinimine complexes
AU  Wei, Pingrong; Chan, Katie T. K.; Stephan, Douglas W.
CS  Department of Chemistry & Biochemistry, University of Windsor, Windsor,
    ON, N9B3P4, Can.
SO  Dalton Transactions (2003), (19), 3804-3810
    CODEN: DTARAF; ISSN: 1477-9226
PB  Royal Society of Chemistry
DT  Journal
LA  English
OS  CASREACT 140:406839
AB  Transmetalation of N-substituted 2-lithiotriphenylphosphine imine
    complexes with boron, aluminum and gallium halides afforded corresponding
    o-metalated triphenylphosphine imide complexes. The reagent
    [(o-C6H4PPh2NSiMe3)Li]2·Et2O (1) reacted with BCl3 affording
    (o-C6H4PPh2:NSiMe3)BCl2 (4). Similarly reaction of 1 with Me2AlCl
    resulted in a 1:1 mixture of (o-C6H4PPh2:NSiMe3)AlMe2 (5) and
    (o-C6H4PPh2NSiMe3)Al(Me)Cl (6) while the analogous reaction of 1 with
    GaCl3 gave (o-C6H4PPh2:NSiMe3)2Ga(o-C6H4PPh2NH) (7). The analogous compound
    [Li(o-C6H4PPh2:NPh)]2·Et2O (2) was used to make
    (o-C6H4PPh2:NPh)GaCl2 (8), while reaction of 2 with Me2AlCl gave a mixture
    of [(o-C6H4PPh2:NPh)AlCl2] (9) and the salt [(o-C6H4PPh2:NPh)2Al][AlMeCl3]
    (10). The compound 2 also reacts with PdCl2(COD) affording
    [Pd(o-C6H4PPh2:NPh)(μ-Cl)]2 (11) and [Pd(o-C6H4PPh2:NPh)2] (12).
    Similarly, the complexes [Ni(o-C6H4PPh2:NPh)2] (13) and
    [Ni(o-C6H4PPh2:N(3,5-C6H3Me2))2] (14) were prepared The compds. 4-14 were
    structurally characterized by x-ray crystallog.
RE.CNT 38  THERE ARE 38 CITED REFERENCES AVAILABLE FOR THIS RECORD
      ALL CITATIONS AVAILABLE IN THE RE FORMAT

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L4  ANSWER 2 OF 79  CAPLUS  COPYRIGHT 2008 ACS on STN
AN  2003:267298  CAPLUS
DN  139:6977

```

TI Salts of the Cation [(Cp\*Cr) $\mu$ -Cl) $\mu$ -CH<sub>2</sub>)<sub>3</sub>AlMe]<sup>+</sup> with the Oxo- and Methine-Based Aluminum Anions [(Me<sub>2</sub>Al) $\mu$ -CH)(AlCl<sub>2</sub>Me)<sub>2</sub>]<sup>-</sup> and [(Me<sub>2</sub>Al)( $\mu$ -O)(AlCl<sub>2</sub>Me)(AlMe<sub>2</sub>Cl)]<sup>-</sup>

AU Wei, Pingrong; Stephan, Douglas W.

CS Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON, N9B 3P4, Can.

SO Organometallics (2003), 22(10), 1992-1994  
CODEN: ORGND7; ISSN: 0276-7333

PB American Chemical Society

DT Journal

LA English

OS CASREACT 139:6977

AB Reactions of (Cp\*CrCl<sub>2</sub>)<sub>2</sub> (1) and Cp\*Cr(HNP-i-Pr<sub>3</sub>)Cl<sub>2</sub> (3) with excess AlMe<sub>3</sub> gave [(Cp\*Cr) $\mu$ -Cl) $\mu$ -CH<sub>2</sub>)<sub>3</sub>AlMe] [(Me<sub>2</sub>Al)( $\mu$ -O)(AlCl<sub>2</sub>Me)(AlMe<sub>2</sub>Cl)] (2) and [(Cp\*Cr) $\mu$ -Cl) $\mu$ -CH<sub>2</sub>)<sub>3</sub>AlMe] [(Me<sub>2</sub>Al) $\mu$ -CH)(AlCl<sub>2</sub>Me)<sub>2</sub>] (4), resp. Although the cations are the same, the former salt has a Al<sub>3</sub>O-based anion, whereas the latter contains an Al<sub>4</sub>-methine anion.

RE.CNT 30 THERE ARE 30 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 3 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 2003:235302 CAPLUS

DN 139:158939

TI Synthesis of amino- and amido-aluminium derivatives and investigation of their dynamics in solution

AU Passarelli, Vincenzo; Carta, Giovanni; Rossetto, Gilberto; Zanella, Pierino

CS ICIS, CNR, Padua, Italy

SO Dalton Transactions (2003), (7), 1284-1291  
CODEN: DTAFA; ISSN: 1477-9226

PB Royal Society of Chemistry

DT Journal

LA English

OS CASREACT 139:158939

AB The salts Li[Al(C<sub>4</sub>H<sub>8</sub>N)<sub>4</sub>] $\cdot$ nC<sub>4</sub>H<sub>8</sub>NH (n = 1, 2; C<sub>4</sub>H<sub>8</sub>NH = pyrrolidine) were prepared and characterized in solution by <sup>1</sup>H-, <sup>13</sup>C-, <sup>7</sup>Li- and <sup>27</sup>Al-NMR spectroscopy. Their reaction with AlCl<sub>3</sub> (Cl/Li molar ratio = 3) affords the binary amido derivative [Al(C<sub>4</sub>H<sub>8</sub>N)<sub>3</sub>]<sub>2</sub>, which, on turn, is reactive towards AlX<sub>3</sub>, yielding [AlX<sub>2</sub>(C<sub>4</sub>H<sub>8</sub>N)]<sub>2</sub> (X = Cl, CH<sub>3</sub>). Binuclear [AlY<sub>2</sub>(C<sub>4</sub>H<sub>8</sub>N)]<sub>2</sub> (Y = Cl, CH<sub>3</sub>, C<sub>4</sub>H<sub>8</sub>N) react with [NH<sub>2</sub>Et<sub>2</sub>]Cl affording the amine complexes AlY<sub>2</sub>Cl(C<sub>4</sub>H<sub>8</sub>NH)<sub>n</sub> (Y = CH<sub>3</sub>, n = 1; Y = Cl, n = 1, 2). Alternatively, the monochloro species AlMe<sub>2</sub>Cl(C<sub>4</sub>H<sub>8</sub>NH) results from the reaction of AlMe<sub>3</sub>(C<sub>4</sub>H<sub>8</sub>NH) and AlCl<sub>3</sub>(C<sub>4</sub>H<sub>8</sub>NH) (CH<sub>3</sub>/Cl molar ratio = 2). The dichloro-Me derivative AlMeCl<sub>2</sub>(C<sub>4</sub>H<sub>8</sub>NH) was obtained by reacting AlMe<sub>3</sub>(C<sub>4</sub>H<sub>8</sub>NH) and AlCl<sub>3</sub>(C<sub>4</sub>H<sub>8</sub>NH) (Cl/CH<sub>3</sub> molar ratio = 2). The Lewis adducts AlCl<sub>3</sub>(amine)<sub>n</sub> (amine = pyrrolidine, n = 1, 2; amine = N,N,N'-trimethylpropanediamine, n = 1) were isolated when AlCl<sub>3</sub> was contacted with the stoichiometric amount of the amine. At variance with N,N,N'-trimethylpropanediamine, N,N,N'-trimethylethylenediamine and N,N,N',N'-tetramethylethylenediamine react with AlCl<sub>3</sub> yielding the salt derivs. [AlCl<sub>2</sub>(amine)<sub>2</sub>][AlCl<sub>4</sub>]. The dynamic processes of the coordinated amine ligands of AlCl<sub>3</sub>(amine)<sub>n</sub> (amine = pyrrolidine, n = 1, 2; amine = N,N,N'-trimethylpropanediamine, n = 1) and [AlCl<sub>2</sub>(amine)<sub>2</sub>][AlCl<sub>4</sub>] (amine = N,N,N',N'-tetramethylethylenediamine) were studied in solution by NMR spectroscopy.

RE.CNT 14 THERE ARE 14 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 4 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 2003:139808 CAPLUS

DN 138:321313

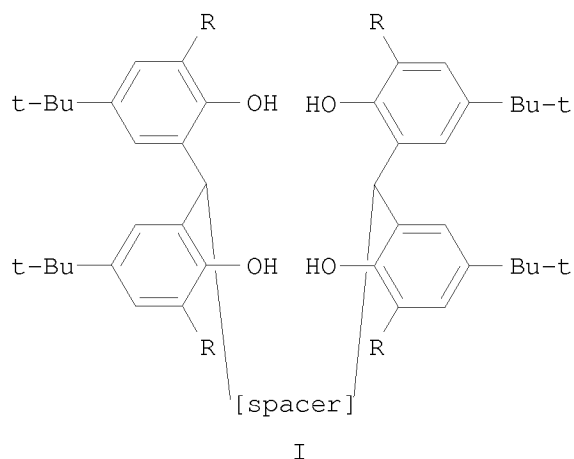
TI Synthesis and Characterization of Organoaluminum Silylamido Complexes

AU Carmalt, Claire J.; Mileham, John D.; White, Andrew J. P.; Williams, David J.  
 CS Department of Chemistry Christopher Ingold Laboratories, University  
 College London, London, WC1H 0AJ, UK  
 SO Organometallics (2003), 22(7), 1554-1557  
 CODEN: ORGND7; ISSN: 0276-7333  
 PB American Chemical Society  
 DT Journal  
 LA English  
 OS CASREACT 138:321313  
 AB The reaction between [Me<sub>2</sub>AlCl] and 1 equiv of HN(SiMe<sub>2</sub>H)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> afforded colorless crystals of [cyclic] [Cl(Me)Al{NH(SiMe<sub>2</sub>H)}]<sub>2</sub> (1). The structure of compound 1 has been determined and shows that the bridging NH(SiMe<sub>2</sub>H) groups adopt a mutually trans arrangement. The related reaction between [Me<sub>2</sub>AlCl] and 1 equivalent of HN(SiMe<sub>2</sub>Ph)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> solution resulted in the isolation of colorless crystals. An x-ray crystallog. study showed that the crystals consist of a mixture of [Cl(Me)<sub>2</sub>Al{NH(SiMe<sub>2</sub>Ph)<sub>2</sub>}] (2) and [Cl<sub>2</sub>(Me)Al{NH(SiMe<sub>2</sub>Ph)<sub>2</sub>}] (3) in a 1:4 ratio. The formation of compound 3 involves the exchange of one of the Me groups attached to the aluminum atom with a chlorine atom.  
 RE.CNT 30 THERE ARE 30 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 5 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 2002:558483 CAPLUS  
 DN 137:328202  
 TI A study on the thermal properties and the solid state pyrolysis of the Lewis acid/base adducts [X<sub>3</sub>M·N(SnMe<sub>3</sub>)<sub>3</sub>] (X = Cl, Br; M = Al, Ga, In) and [Cl<sub>2</sub>MeM·N(SnMe<sub>3</sub>)<sub>3</sub>] (M = Al, Ga) as molecular precursors for group 13 nitride materials  
 AU Cheng, Q. M.; Stark, O.; Stowasser, F.; Wohlfart, A.; Fischer, R. A.  
 CS Lehrstuhl fuer Anorganische Chemie II - Organometallics & Materials Chemistry, Ruhr-Universitaet Bochum, Bochum, D-44780, Germany  
 SO Journal of Materials Chemistry (2002), 12(8), 2470-2474  
 CODEN: JMACEP; ISSN: 0959-9428  
 PB Royal Society of Chemistry  
 DT Journal  
 LA English  
 AB The Lewis acid/base adducts [X<sub>3</sub>M·N(SnMe<sub>3</sub>)<sub>3</sub>] (compds. 1-3: X = Cl, Br; M = Al, Ga, In) and [Cl<sub>2</sub>MeM·N(SnMe<sub>3</sub>)<sub>3</sub>] (compound 4: M = Al, compound 5: M = Ga) were studied as precursors for group 13 nitride materials. The compds. were prepared by the 1:1 mol reaction of MX<sub>3</sub> and MCl<sub>2</sub>Me with N(SnMe<sub>3</sub>)<sub>3</sub> at room temperature in di-Et ether and crystallized from CH<sub>2</sub>Cl<sub>2</sub> at -20°C. As shown by thermal anal. and the anal. of the volatile byproducts, the precursors of the type [X<sub>3</sub>M·N(SnMe<sub>3</sub>)<sub>3</sub>] decompose between 100 and 350°C predominantly in two steps via dehalostannylation by partly releasing Me<sub>3</sub>SnCl. Polycryst. powders of AlN, GaN and InN were obtained after prolonged pyrolysis under inert conditions (argon, and in vacuo) at >350°C and were contaminated with metallic tin according to the X-ray powder diffraction patterns. The pyrolysis of the organometallic precursors [Cl<sub>2</sub>MeM·N(SnMe<sub>3</sub>)<sub>3</sub>] (preceramic compds. 4 and 5) yielded tin-free nitride materials at <350°C due to the parallel elimination of SnMe<sub>4</sub> and Me<sub>3</sub>SnCl, as evidenced by X-ray powder diffraction, elemental anal., NMR and IR spectroscopy of the products.  
 RE.CNT 49 THERE ARE 49 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 6 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 2002:556601 CAPLUS  
 DN 137:263089

TI Synthesis and Reactivity of Bi-, Tri-, and Tetrametallic Aluminum  
 Tetraphenolate Complexes  
 AU Cottone, Andrew, III; Scott, Michael J.  
 CS Department of Chemistry and Center for Catalysis, University of Florida,  
 Gainesville, FL, 32611-7200, USA  
 SO Organometallics (2002), 21(17), 3610-3627  
 CODEN: ORGND7; ISSN: 0276-7333  
 PB American Chemical Society  
 DT Journal  
 LA English  
 OS CASREACT 137:263089  
 GI



AB A series of ligands, each with four phenoxide arms, have been prepared with the intent to place two Lewis acidic metal center in close proximity and thus foster cooperative binding of external Lewis bases. The ligands, I [1-5; spacer = anthracene, R = t-Bu (1H4), spacer = dibenzofuran, R = t-Bu (2H4), spacer = xanthene, R = t-Bu (3H4), spacer = dibenzofuran, R = Me (4H4), spacer = anthracene, R = iPr (5H4)], incorporate a pair of 2,2'-methylenebis(4-tert-butyl-6-alkylphenol) groups linked by three different spacers: anthracene (1H4, 5H4), dibenzofuran (2H4, 4H4), and xanthene (3H4). The reaction of 1H4 and 2H4 with trimethylaluminum led to the formation of the C2-sym., tetranuclear aluminum compds. [(1)Al<sub>4</sub>Me<sub>8</sub>], 6, and [(2)Al<sub>4</sub>Me<sub>8</sub>], 7, resp. In contrast, when 3H4 was treated with trimethylaluminum, a binuclear aluminum species, [(3)Al<sub>2</sub>Me<sub>2</sub>], 8, containing an Al<sub>2</sub>O<sub>2</sub> bridging unit, was isolated. Heating solns. of the tetranuclear complexes 6 and 7 in the presence of excess ligand induced the elimination of 2 equivalent of trimethylaluminum and afforded the binuclear aluminum complexes [(1)Al<sub>2</sub>Me<sub>2</sub>], 9, and [(2)Al<sub>2</sub>Me<sub>2</sub>], 10. Addition of NEt<sub>4</sub>Cl to solns. of 9 and 10 resulted in the isolation of the anionic, bimetallic aluminum species [NEt<sub>4</sub>][(1)Al<sub>2</sub>Me<sub>2</sub>Cl], 11, and [NEt<sub>4</sub>][(2)Al<sub>2</sub>Me<sub>2</sub>Cl], 12. Both complexes contain a sym. chloride bridge between the two metal centers. In contrast, the reaction of NEt<sub>4</sub>Cl with 8 produced the asym. dianionic compound [NEt<sub>4</sub>]<sub>2</sub>[(3)Al<sub>2</sub>Me<sub>2</sub>Cl<sub>2</sub>], 13. Compound 9 reacts with sodium phenoxide to afford [(1)Al<sub>2</sub>Me<sub>2</sub>(OPh)Na(OEt<sub>2</sub>)], 14, and this species contains a six-membered NaAl<sub>2</sub>O<sub>3</sub> ring. When ketones or aldehydes are added to 9, the two aluminum centers in the resulting product each bind a carbonyl group in an η<sup>1</sup> fashion. For example, the reaction of α,α,α-trimethylacetophenone with 9 produced the C2-sym. complex {(1)[AlMe(OC<sub>11</sub>H<sub>14</sub>)]<sub>2</sub>}, 15, while 10, upon addition of cyclopentanone, afforded the asym., monometallic species [(2H)Al(OC<sub>5</sub>H<sub>8</sub>)], 16, with one free phenolic arm. The three remaining phenoxide groups in 16 all

coordinate to the lone aluminum. To probe the influence of the steric environment of the ligand on the reactivity, Me groups were incorporated at the ortho-position of the phenoxide, and this ligand, 4H4, reacted with trimethylaluminum to produce the trinuclear species [(4)Al<sub>3</sub>Me<sub>5</sub>], 17, with a stabilizing six-membered Al<sub>3</sub>O<sub>3</sub> bridge. The slightly more sterically encumbered isopropyl-substituted ligand, 5H4, formed the binuclear aluminum species [(5)Al<sub>2</sub>Me<sub>2</sub>], 18, analogous to 8, 9, and 10. Addition of benzaldehyde to 18 afforded the asym. binuclear species {(5)[AlMe][AlMe(OCHPh)]}, 19, and the benzaldehyde substrate coordinates to only one aluminum in this complex. The crystal structures of all the compds. prepared were determined

RE.CNT 77 THERE ARE 77 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 7 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 2002:527073 CAPLUS

DN 137:384917

TI Lewis base properties of tris(trimethylstannyl)amine: unusually short M-N bonds of the adduct compounds [X<sub>3</sub>M·N(SnMe<sub>3</sub>)<sub>3</sub>] (X = Cl, Br; M = Al, Ga, In) and [Cl<sub>2</sub>(CH<sub>3</sub>)M·N(SnMe<sub>3</sub>)<sub>3</sub>] (M = Al, Ga)

AU Cheng, Q. M.; Stark, O.; Merz, K.; Winter, M.; Fischer, R. A.

CS Lehrstuhl fuer Anorganische Chemie II - Organometallics & Materials Chemistry, Ruhr-Universitaet Bochum, Bochum, D-44780, Germany

SO Journal of the Chemical Society, Dalton Transactions (2002), (14), 2933-2936

CODEN: JCSDA; ISSN: 1472-7773

PB Royal Society of Chemistry

DT Journal

LA English

AB The Lewis acid/base adducts [X<sub>3</sub>M·N(SnMe<sub>3</sub>)<sub>3</sub>] (1a: M = Al, X = Cl; 2a: M = Ga, X = Cl; 2b: M = Ga, X = Br; 3a: M = In, X = Cl; 3b: M = In, X = Br) and [Cl<sub>2</sub>MeM·N(SnMe<sub>3</sub>)<sub>3</sub>] (1b: M = Al, 2c: M = Ga) were prepared by 1 : 1 mol reaction of MX<sub>3</sub> and MCl<sub>2</sub>Me with N(SnMe<sub>3</sub>)<sub>3</sub> at room temperature in di-Et ether and crystallized from dichloromethane at -20°. The new compds. were fully characterized by elemental anal., NMR spectroscopy and single crystal x-ray diffraction. Unusually short M-N bond lengths of 1.87(1) Å for Al-N (1a), 1.950(7) Å for Ga-N (2a) and 2.148(6) Å for In-N (3a) were found indicating very strong donor-acceptor bonds.

RE.CNT 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 8 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 2002:306300 CAPLUS

DN 137:33402

TI One-Pot Synthesis of (η<sup>6</sup>-Arene)bis(triphenylphosphine)(methyl)ruthenium(II) Cations. X-ray Structures of [(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)Ru(Me)(PPh<sub>3</sub>)<sub>2</sub>][AlCl<sub>2</sub>Me<sub>2</sub>] and the η<sup>5</sup>-Thiophene Analogue

AU Fang, Xinggao; Watkin, John G.; Scott, Brian L.; John, Kevin D.; Kubas, Gregory J.

CS Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM, 87545, USA

SO Organometallics (2002), 21(11), 2336-2339

CODEN: ORGND7; ISSN: 0276-7333

PB American Chemical Society

DT Journal

LA English

OS CASREACT 137:33402

AB The authors report 1-pot syntheses for complexes [(η<sup>6</sup>-arene)RuIIME(PPh<sub>3</sub>)<sub>2</sub>][AlCl<sub>2</sub>Me<sub>2</sub>] in high yields and x-ray structures of the η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub> and η<sup>5</sup>-thiophene derivs. Other derivs. include fluorobenzene and mesitylene complexes, and all of the complexes were

synthesized by addition of AlMe<sub>3</sub> to RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> in the neat arene solvent or in an admixt. with hexane for thiophene and fluorobenzene. The crystal and mol. structures of [(arene)Ru(Me)(PPh<sub>3</sub>)<sub>2</sub>][AlCl<sub>2</sub>Me<sub>2</sub>]·CH<sub>2</sub>Cl<sub>2</sub> (arene = η<sup>6</sup>-benzene, η<sup>5</sup>-thiophene) were determined by x-ray crystallog.

RE.CNT 24 THERE ARE 24 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 9 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 2001:746733 CAPLUS

DN 138:321349

TI Carbon-carbon bond formation via oxidative-addition processes of titanium(II) reagents with π-bonded organic substrates. Reactivity modifications by Lewis acids and Lewis bases. Part 22. Organic chemistry of subvalent transition metal complexes. [Erratum to document cited in CA135:107419]

AU Eisch, J. J.; Gitua, J. N.; Otieno, P. O.; Shi, X.

CS Department of Chemistry, The State University of New York at Binghamton, Binghamton, NY, 13902-6016, USA

SO Journal of Organometallic Chemistry (2001), 634(2), 214

CODEN: JORCAI; ISSN: 0022-328X

PB Elsevier Science S.A.

DT Journal

LA English

AB On page 233, Section 2.2.3, paragraph 2, lines 9-10, the word "benzpinacol" should be "benzopinacole". On page 237, Section 5.6, line 5, the phrase "... to consist of 95% cis-stilbene, 5% of..." should be written as "... to consist of 95% benzhydrol, 3% of...". On page 237, Section 5.6, line 6, the phrase "... and <1% of benzpinacol and..." should be written as "... and <2% of benzopinacole and...".

L4 ANSWER 10 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 2001:295197 CAPLUS

DN 135:107419

TI Carbon-carbon bond formation via oxidative-addition processes of titanium(II) reagents with π-bonded organic substrates. Reactivity modifications by Lewis acids and Lewis bases Part 22. Organic chemistry of subvalent transition metal complexes

AU Eisch, J. J.; Gitua, J. N.; Otieno, P. O.; Shi, X.

CS Department of Chemistry, The State University of New York at Binghamton, Binghamton, NY, 13902-6016, USA

SO Journal of Organometallic Chemistry (2001), 624(1-2), 229-238

CODEN: JORCAI; ISSN: 0022-328X

PB Elsevier Science S.A.

DT Journal

LA English

OS CASREACT 135:107419

AB A series of titanium(II) derivs., TiE<sub>2</sub>, was prepared by alkylative reduction of TiE<sub>4</sub> by two equivalent of n-butyllithium in THF at -78 to 25° (E = Cl, F, OBun, OPri, 0.5 NPh-CH<sub>2</sub>-CH<sub>2</sub>-NPh). The LiE byproduct could usually be removed by THF evaporation and dissoln. of the TiE<sub>2</sub> into toluene. All such TiE<sub>2</sub> derivs. were shown to effect the epimetalation and oligomerization of olefins, acetylenes and carbonyl derivs. in varying degrees. Particularly pertinent were the isolation and chemical reactions of titanium(II) isopropoxide, the postulated intermediate in the Kulinkovich synthesis of cyclopropanols from Et Grignard reagents and organic esters, as well as an intermediate in many allied reactions developed by the Sato group. The findings of the present study corroborate completely the foregoing hypothesis that titanium(II) isopropoxide is the key intermediate in such novel reactions in organic synthesis. Furthermore, Ti(OPri)<sub>2</sub> can be prepared readily in a relatively pure state and has been found to react with 1-alkenes, alkynes and ketones by epimetalation at 25° to form three-membered titanacycles, which can be utilized in organic synthesis.

Finally, the ease with which such  $TiE_2$  derivs. epimetalate unsatd. organic substrates has been decreased by the steric demands of E and by the coordination of Lewis bases or donor solvent to the titanium(II) center. Lewis acids, on the other hand, greatly increase the rate of epimetalation by  $TiE_2$ . A dramatic illustration of this effect is in the action of  $TiCl_2 \cdot Me_2AlCl$  on unsatd. hydrocarbons, wherein the polymerization of ethylene and of 1-alkene and the cyclotrimerization of alkynes are found to occur at room temperature

RE.CNT 23 THERE ARE 23 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 11 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
AN 2001:250145 CAPLUS  
DN 135:61377  
TI The variable reaction behaviour of base-free [tris(trimethylsilyl)methyl]lithium with trihalides of earth metals and iron  
AU Viefhaus, T.; Schwarz, W.; Hubler, K.; Locke, K.; Weidlein, J.  
CS Inst. fur Anorganische Chemie, Univ. Stuttgart, Stuttgart, Germany  
SO Zeitschrift fuer Anorganische und Allgemeine Chemie (2001), 627(4), 715-725  
CODEN: ZAACAB; ISSN: 0044-2313  
PB Wiley-VCH Verlag GmbH  
DT Journal  
LA German  
OS CASREACT 135:61377  
AB Base-free  $(Me_3Si)_3CLi$  (Tsi-Li) reacts with  $MHal_3$  ( $M = Al, Ga, In$ ;  $Hal = Cl, Br, I$ ) primarily to give the resp. metalates  $[Tsi-MHal_3]Li$ . Simultaneously to this simple metathesis, a methylation also takes place, mainly with heavier halides of Ga and In with excess Tsi-Li, forming the mono and di-Me compds.  $Tsi-M(Me)I$  ( $M = Ga, In$ ),  $Tsi-GaMe_2$ , and  $(Tsi)_2InMe$ , resp., as well as the main byproduct 1,3-disilacyclobutane. Representatives of each type of compound were isolated by fractional crystallization or sublimation and were characterized by spectroscopy ( $^1H$ ,  $^{13}C$  and  $^{29}Si$  NMR, IR, Raman) and x-ray elucidations. Reduction takes place when  $FeCl_3$  reacts with Tsi-Li (1:3 ratio) in toluene at  $55-60^\circ$ , yielding red-violet  $Fe(Tsi)_2$ ,  $(Me_3Si)_3CCH_2Ph$ , and low amts. of Tsi-Cl.  $Fe(Tsi)_2$  is monomeric, crystallizes in the monoclinic space group  $C2/c$  and consists of a linear C-Fe-C skeleton with  $d(Fe-C) = 204.5(4)$  pm.

RE.CNT 45 THERE ARE 45 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 12 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
AN 2001:85092 CAPLUS  
DN 134:295927  
TI Coordination of Lewis Acid to  $\eta^2$ -Enonepalladium(0) Leading to Continuous Structure Variation from  $\eta^2$ -Olefin Type to  $\eta^3$ -Allyl Type  
AU Ogoshi, Sensuke; Yoshida, Tomohiro; Nishida, Takuma; Morita, Masaki; Kurosawa, Hideo  
CS Department of Applied Chemistry Faculty of Engineering, Osaka University, Suita Osaka, 565-0871, Japan  
SO Journal of the American Chemical Society (2001), 123(9), 1944-1950  
CODEN: JACSAT; ISSN: 0002-7863  
PB American Chemical Society  
DT Journal  
LA English  
OS CASREACT 134:295927  
AB The reaction of  $\alpha, \beta$ -unsatd. carbonyl compds., a  $Pd(0)$  complex, and Lewis acids gave a new class of complexes showing a wide variety of structures with  $\eta^2$ -type and  $\eta^3$ -type coordination of the carbonyl



compds. The reaction of  $\text{Pd}(\text{PhCH:CHCOCH}_3)(\text{PPh}_3)_2$  with  $\text{BF}_3 \cdot \text{OEt}_2$  or  $\text{B}(\text{C}_6\text{F}_5)_3$  quant. gave Pd complexes 1a,b having  $\text{BX}_3$ -coordinated  $\eta^2$ -enonepalladium structure, as revealed by x-ray structure anal. of the  $\text{B}(\text{C}_6\text{F}_5)_3$  adduct 1b. However, the reaction of  $\text{Pd}(\text{PhCH:CHCHO})(\text{PPh}_3)_2$  with  $\text{BF}_3 \cdot \text{OEt}_2$  or  $\text{B}(\text{C}_6\text{F}_5)_3$  gave distorted zwitterionic  $\eta^3$ -allylpalladium complexes 3a,b, where the Pd-carbonyl C distance in 3a (2.413(4) Å) is much shorter than that (2.96(1) Å) in 1b. The values of the P-P coupling constant and  $^{13}\text{C}$  chemical shift for carbonyl C are useful criteria for predicting how the  $\eta^3$ -coordination mode contributes to the structure of the enone-Pd-Lewis acid system. MO calcns. on model complexes suggest that orbital overlap in the HOMO between the Pd and carbonyl C is enlarged by coordination of the Lewis acid to the carbonyl group. Pd-catalyzed conjugate addition of R-M (R-M =  $\text{AlMe}_3$ ,  $\text{AlEt}_3$ ,  $\text{ZnEt}_2$ ) and its plausible reaction path are also reported.

RE.CNT 32 THERE ARE 32 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 13 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
AN 2000:742861 CAPLUS  
DN 134:42178  
TI Synthesis and purification of trimethylgallium for MOCVD: molecular structure of  $(\text{KF})_4 \cdot 4(\text{Me}_3\text{Ga})$   
AU Starowieyski, Kazimierz B.; Chwojnowski, Andrzej; Jankowski, Krzysztof; Lewinski, Janusz; Zachara, Janusz  
CS Faculty of Chemistry, Warsaw University of Technology, Warsaw, 00-662, Pol.  
SO Applied Organometallic Chemistry (2000), 14(10), 616-622  
CODEN: AOCHEX; ISSN: 0268-2605  
PB John Wiley & Sons Ltd.  
DT Journal  
LA English  
OS CASREACT 134:42178  
AB Trimethylgallium was obtained from a 3:1 M mixture of  $\text{Me}_2\text{AlCl}$  (1) and  $\text{GaCl}_3$  (2) only in the presence of  $\text{NaCl}$ . The mechanism of the reaction was traced. It is postulated that the gallium-aluminum dimers  $\text{Cl}_n\text{Me}_2\text{-nAlCl}_2$   $\text{GaCl}_m\text{Me}_2\text{-m}$  (m and n = 0, 1 or 2), formed in consecutive alkylation steps, do not participate in further alkyl-chlorine exchange.  $\text{NaCl}$  splits the dimers that form the precipitate of  $\text{Na}[\text{MeAlCl}_3]$  (3), thus liberating  $\text{Me}_n\text{GaCl}_3\text{-n}$  which, on further alkylation by  $\text{Me}_2\text{AlCl}$ , finally yields  $\text{Me}_3\text{Ga}$ . For an MOCVD application, it is purified through a complex with  $\text{KF}$ , which under vacuum decomp. at 180-300°C, to yield a product contaminated by less than 1 ppm of the total impurities. The x-ray study of the complex reveals a tetrameric, highly sym. heterocubane of formula  $(\text{KF})_4 \cdot 4(\text{Me}_3\text{Ga})$ .

RE.CNT 41 THERE ARE 41 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 14 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
AN 2000:663063 CAPLUS  
DN 134:4969  
TI Group 13 Cation Formation with a Potentially Tridentate Ligand  
AU Munoz-Hernandez, Miguel-Angel; Keizer, Timothy S.; Parkin, Sean; Patrick, Brian; Atwood, David A.  
CS Department of Chemistry, The University of Kentucky, Lexington, KY, 40506-0055, USA  
SO Organometallics (2000), 19(21), 4416-4421  
CODEN: ORGND7; ISSN: 0276-7333  
PB American Chemical Society  
DT Journal  
LA English  
OS CASREACT 134:4969  
AB A potentially tridentate ligand, 3,5-tBu<sub>2</sub>-2-HOC<sub>6</sub>H<sub>2</sub>CH:NC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-2

(Phensal(tBu)H<sub>3</sub>), was prepared by the condensation of 1 equiv of phenylenediamine with 3,5-di-tert-butylsalicylaldehyde. When 1 equiv of this new ligand was added to AlMe<sub>3</sub>, [[Phensal(tBu)HAlMe]<sub>2</sub>] (1) results. In contrast, this reaction with GaMe<sub>3</sub> produces [Phensal(tBu)H<sub>2</sub>]GaMe<sub>2</sub> (2). When 1 or 2 equiv of Phensal(tBu)H<sub>3</sub> is combined with Et<sub>2</sub>AlCl, [Phensal(tBu)H<sub>2</sub>]2AlCl (3) forms. However the same reaction with Me<sub>2</sub>GaCl leads to [Phensal(tBu)H<sub>2</sub>]Ga(Me)Cl (4). A cationic complex, {[Phensal(tBu)H<sub>2</sub>]2Al}+Cl<sup>-</sup> (5), is formed when 3 is dissolved in MeOH. The MeOH apparently mediates the formation of the cation but does not coordinate the cationic metal. When the solvent is removed, 5 reverts back to neutral 3. When 3 is combined with GaCl<sub>3</sub> in toluene, another cationic complex, {[Phensal(tBu)H<sub>2</sub>]2Al}+GaCl<sub>4</sub><sup>-</sup> (6), is formed. In a similar manner, {[Phensal(tBu)H<sub>2</sub>]2Al}+Me<sub>2</sub>AlCl<sub>2</sub><sup>-</sup> (7) is formed by adding Me<sub>2</sub>AlCl to 3. The compds. were characterized by m.p., elemental analyses, IR, <sup>1</sup>H and <sup>27</sup>Al NMR, and in the case of 2, 5, and 6 single-crystal x-ray anal.

RE.CNT 41      THERE ARE 41 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4    ANSWER 15 OF 79    CAPLUS    COPYRIGHT 2008 ACS on STN  
AN    2000:249054    CAPLUS  
DN    132:356046  
TI    Reactions of alkylaluminium chlorides with diols. Crystal structure of C<sub>15</sub>Al<sub>3</sub>[OC(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>O]<sub>2</sub>  
AU    Ziemkowska, Wanda; Pasynkiewicz, Stanislaw; Anulewicz-Ostrowska, Romana; Fraczak, Michal  
CS    Faculty of Chemistry, Warsaw University of Technology, Warsaw, 00-662, Pol.  
SO    Main Group Metal Chemistry (2000), 23(3), 169-178  
CODEN: MGMCE8; ISSN: 0792-1241  
PB    Freund Publishing House Ltd.  
DT    Journal  
LA    English  
AB    The reaction of 2,4-dimethyl-2,4-pentanediol with the mixture of Me<sub>2</sub>AlCl and MeAlCl<sub>2</sub> at 2:0.75:2.25 molar ratio of reactants proceeded yielding the complex C<sub>15</sub>Al<sub>3</sub>[OCMe<sub>2</sub>CH<sub>2</sub>CMe<sub>2</sub>O]<sub>2</sub> (1). The pure complex 1 was isolated and characterized by <sup>1</sup>H, <sup>27</sup>Al NMR spectroscopy, mol. weight measurements and elemental anal. The crystal structure of 1 was determined by x-ray diffraction anal. However, the reaction of 2,4-dimethyl-2,4-pentanediol with Me<sub>2</sub>AlCl at 2:3 molar ratio of reagents gave the crystalline inseparable mixture of complexes MenC<sub>15</sub>-nAl<sub>3</sub>[OCMe<sub>2</sub>CH<sub>2</sub>CMe<sub>2</sub>O]<sub>2</sub> [n = 0-4] (2). The crystal structure of the product 2 was determined by x-ray diffraction study.

RE.CNT 22      THERE ARE 22 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4    ANSWER 16 OF 79    CAPLUS    COPYRIGHT 2008 ACS on STN  
AN    2000:213045    CAPLUS  
DN    132:308386  
TI    The correlation of dative bond length and parameter n in adducts Me<sub>3</sub>N-AlMe<sub>3</sub>-nCl<sub>n</sub> (n ≤ 3)  
AU    Gelbrich, T.; Sieler, J.; Dumichen, U.  
CS    Department of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK  
SO    Zeitschrift fuer Kristallographie (2000), 215(2), 127-130  
CODEN: ZEKRDZ; ISSN: 0044-2968  
PB    R. Oldenbourg Verlag  
DT    Journal  
LA    English  
AB    Complexes Me<sub>3</sub>N-AlMe<sub>3</sub>-nCl<sub>n</sub> (n = 0, 1, 2, 3) were synthesized in 84-89% yields by reaction of Me<sub>3</sub>N with the corresponding AlMe<sub>3</sub>-nCl<sub>n</sub> in pentane or Et<sub>2</sub>O and structurally characterized by x-ray crystallog. and NMR spectroscopy. The shape of the mols. is trigonal-antiprismatic with the N

and Al atoms being tetrahedrally surrounded. The length of the dative bond N-Al is correlated with the parameter n due to inductive effects of the electroneg. Cl substituents, resulting in a difference in N-Al between all complexes of 0.1 Å (2.045, 2.010, 1.971, and 1.949 Å). This shortening with increasing n, however, is not linear.

RE.CNT 13      THERE ARE 13 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4      ANSWER 17 OF 79    CAPLUS    COPYRIGHT 2008 ACS on STN

AN      2000:140339    CAPLUS

DN      132:308382

TI      Bimetallic and cationic aluminum with N3O2 chelate ligands

AU      Liu, Shengming; Munoz-Hernandez, Miguel-Angel; Atwood, David A.

CS      Department of Chemistry, The University of Kentucky, Lexington, KY, USA

SO      Journal of Organometallic Chemistry (2000), 596(1-2), 109-114

CODEN: JORCAI; ISSN: 0022-328X

PB      Elsevier Science S.A.

DT      Journal

LA      English

AB      The ligands aminobis(N-ethylenesalicylideneimine) (SalenN3H3) and aminobis(N-propylenesalicylideneimine) (SalpenN3H3) were used to form the bimetallic complexes SalenN3H{AlMe2}2 (1), SalpenN3H{AlMe2}2 (2), SalenN3H{AlMeCl}2 (3) and SalpenN3H{AlMeCl} (4). When extracted in THF 3 and 4 redistribute to form the ionic compds. [SalenN3H{Al(THF)}]+ [AlMe2Cl2]- (5) and [SalpenN3H{Al(THF)}]+ [AlMe2Cl2]- (6). The compds. were characterized by Mp analyses, 1H-NMR and IR, and in the case of 2 and 6 by x-ray crystallog. Addnl., the potential of 5 and 6 to serve as propylene oxide polymerization catalysts was examined

RE.CNT 29      THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4      ANSWER 18 OF 79    CAPLUS    COPYRIGHT 2008 ACS on STN

AN      2000:20838    CAPLUS

DN      132:180614

TI      Synthesis, properties, and molecular structures of alkylaluminum aminoalkoxide chlorides

AU      Hecht, Elmar; Gelbrich, Thomas; Thiele, Karl-Heinz; Sieler, Joachim

CS      Inst. Anorganische Chemie, Univ. Leipzig, Leipzig, Germany

SO      Zeitschrift fuer Anorganische und Allgemeine Chemie (2000), 626(1), 180-186

CODEN: ZAACAB; ISSN: 0044-2313

PB      Wiley-VCH Verlag GmbH

DT      Journal

LA      German

OS      CASREACT 132:180614

AB      Alkylaluminum aminoalkoxide chlorides R(Cl)AlOR\* [R = Et, R\* = (CH2)3NMe2 (1); R = Me, R\* = CHMeCH2NMe2; R = Me, R\* = (S)-N-methyl-2-pyrrolidinylmethyl] were obtained from the reaction of R2AlCl with the resp. amino alc. R\*OH. The reaction between Me2AlCl and (S)- $\alpha,\alpha$ -diphenyl-2-pyrrolidinemethanol (dpm-H) yielded, by contrast, the ionic {[MeAl(dpm)2AlMe2]+[MeAlCl3]-} complex (4). The new compds. were characterized by 1H, 13C, and 27Al NMR. Crystal structures of 1 and 4.OEt2 were determined by x-ray methods, and the absolute structure of 4 was confirmed by refinement of the Flack parameter. The dimeric mols. of 1 are composed of 2 chelating rings linked via an almost planar Al2O2 unit, and pentacoordination is observed about Al. In contrast, each of the 2 crystallog. independent cation mols. of 4 contains one 4- and one 5-coordinate metal center.

RE.CNT 34      THERE ARE 34 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 19 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1999:574285 CAPLUS  
 DN 131:322667  
 TI Neutral and Cationic Group 13 Phosphinimine and Phosphinimide Complexes  
 AU Ong, Christopher M.; McKarns, Peggy; Stephan, Douglas W.  
 CS Department of Chemistry and Biochemistry School of Physical Sciences,  
 University of Windsor, Windsor, ON, N9B 3P4, Can.  
 SO Organometallics (1999), 18(20), 4197-4204  
 CODEN: ORGND7; ISSN: 0276-7333  
 PB American Chemical Society  
 DT Journal  
 LA English  
 OS CASREACT 131:322667  
 AB Reactions of the silylphosphimines R<sub>3</sub>PNSiMe<sub>3</sub> (R = i-Pr, Ph, Cy) with  
 AlCl<sub>3</sub>, AlMeCl<sub>2</sub>, AlMe<sub>2</sub>Cl, and AlMe<sub>3</sub> afford the compds. (i-Pr<sub>3</sub>PNSiMe<sub>3</sub>)AlCl<sub>3</sub>  
 (1), (R<sub>3</sub>PNSiMe<sub>3</sub>)AlMeCl<sub>2</sub> (R = i-Pr, 2; Ph, 3; Cy, 4), (R<sub>3</sub>PNSiMe<sub>3</sub>)AlMe<sub>2</sub>Cl (R  
 = i-Pr, 5; Ph, 6; Cy, 7), and (R<sub>3</sub>PNSiMe<sub>3</sub>)AlMe<sub>3</sub> (R = i-Pr, 8; Ph, 9; Cy,  
 10). Reaction of R<sub>3</sub>PNH (R = t-Bu, Cy, Ph) with AlMe<sub>2</sub>Cl and AlMe<sub>3</sub> afforded  
 (R<sub>3</sub>PNH)AlMe<sub>2</sub>Cl (R = Cy, 11; t-Bu, 12) and (Ph<sub>3</sub>PNH)AlMe<sub>3</sub> (13), resp. The  
 dimeric species [Me<sub>2</sub>Al(μ-NPt-Bu<sub>3</sub>)]<sub>2</sub> (14) [AlCl<sub>2</sub>(μ-NPt-Bu<sub>3</sub>)]<sub>2</sub> (15)  
 were derived from reactions of (t-Bu<sub>3</sub>PNH) and AlMe<sub>3</sub> and t-Bu<sub>3</sub>PNLi and  
 MeAlCl<sub>2</sub>, resp. Reaction of the bisphosphinimine salt LiCH(PPh<sub>2</sub>(NSiMe<sub>3</sub>))<sub>2</sub>  
 (16) with aluminum, gallium, and indium halides yielded  
 [CH(PPh<sub>2</sub>(NSiMe<sub>3</sub>))<sub>2</sub>]MCl<sub>2</sub> (M = Al, 17; Ga, 18; In, 19) while the analogous  
 species [CH(PPh<sub>2</sub>(NSiMe<sub>3</sub>))<sub>2</sub>]AlMe<sub>2</sub> (20) was prepared via reaction of 16 with  
 Me<sub>2</sub>AlCl. The compds. [CH(PPh<sub>2</sub>(NSiMe<sub>3</sub>))<sub>2</sub>]MR<sub>2</sub> (M = Al, Bz, 21; M = Ga, R =  
 Me, 22; Bz, 23; M = In, R = Me, 24; Bz, 25) were readily prepared by  
 treatment of 17-19 with the appropriate alkylating reagents. The borane  
 B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> reacts stoichiometrically with the adducts 8-10 to give the  
 products [(R<sub>3</sub>PNSiMe<sub>3</sub>)AlMe<sub>2</sub>][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (R = i-Pr, 26; Ph, 27; Cy, 28)  
 while treatment of 27 with PMe<sub>3</sub> affords clean conversion to the salt  
 [(Ph<sub>3</sub>PNSiMe<sub>3</sub>)<sub>2</sub>AlMe(PMe<sub>3</sub>)][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (29). Similarly, species  
 [Me<sub>2</sub>Al(μ-NPt-Bu<sub>3</sub>)<sub>2</sub>AlMe][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (30) and [Me<sub>2</sub>Al(μ-NPt-  
 Bu<sub>3</sub>)<sub>2</sub>AlMe(PMe<sub>3</sub>)][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (31) were obtained from 14. Attempts to  
 generate the related ionic derivs. from 20-25 yielded unstable mixts. of  
 products. Under mild conditions these group 13 ionic species did not  
 effect the polymerization of ethylene. Crystallog. data are reported for  
 compds.  
 1, 3, 6, 8, 11, 13-15, 18, and 20.  
 RE.CNT 31 THERE ARE 31 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 20 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1999:357005 CAPLUS  
 DN 131:116321  
 TI Reactivity of AlMe<sub>3</sub> with titanium(IV) Schiff base complexes: X-ray  
 structure of [Ti{(μ-Br)(AlMe<sub>2</sub>)}{(μ-Br)(AlMe<sub>2</sub>X)}(salen)].C<sub>7</sub>H<sub>8</sub> (X = Me  
 or Br) and reactivity studies of mono-alkylated [Ti(Me)X(L)] complexes  
 AU Coles, Simon J.; Hursthouse, Michael B.; Kelly, David G.; Toner, Andrew  
 J.; Walker, Neil M.  
 CS Department of Chemistry, University of Wales College of Cardiff, Cardiff,  
 CF1 3TB, UK  
 SO Journal of Organometallic Chemistry (1999), 580(2), 304-312  
 CODEN: JORCAI; ISSN: 0022-328X  
 PB Elsevier Science S.A.  
 DT Journal  
 LA English  
 OS CASREACT 131:116321  
 AB [TiCl<sub>2</sub>(salen)] (1) reacts with AlMe<sub>3</sub> (1:2) to give the heterometallic  
 Ti(III) and Ti(IV) complexes [Ti{(μ-Cl)(AlMe<sub>2</sub>)}{(μ-  
 Cl)(AlMe<sub>2</sub>X)}(salen)] (X = Me or Cl) and [TiMe{(μ-Cl)(AlCl<sub>2</sub>Me)}(salen)]  
 (3). Addition of Et<sub>2</sub>O to 3 affords [Ti(Me)Cl(salen)] (4). The analogous

reaction of [TiBr<sub>2</sub>(salen)] gives the crystallog. characterized [Ti{(μ-Br)(AlMe<sub>2</sub>)}{(μ-Br)(AlMe<sub>2</sub>X)}(salen)] (X = Me or Br) and [Ti(Me)Br(salen)] in a single step, while the comparable reaction of [TiCl<sub>2</sub>{(3-MeO)<sub>2</sub>salen}] with AlMe<sub>3</sub> yields [Ti(Me)Cl{(3-MeO)<sub>2</sub>salen}] with no evidence of Ti(III) species. Reactivity of both halide and Me groups of 4 was probed using Mg reduction, SbCl<sub>5</sub> and AgBF<sub>4</sub> halide abstraction and SO<sub>2</sub> insertion reactions. Hydrolysis of [Ti(Me)X(L)] complexes affords μ-oxo species [TiX(L)]<sub>2</sub>(μ-O) [X = Cl, L = salen; X = Br, L = salen; X=Cl, L = (3-MeO)<sub>2</sub>salen].

RE.CNT 38 THERE ARE 38 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 21 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
AN 1999:109179 CAPLUS  
DN 130:290589  
TI Stereochemical control of cis- and trans-TiCl<sub>2</sub> groups in six-coordinate complexes [(L)TiCl<sub>2</sub>] (L<sub>2</sub>- = N<sub>2</sub>O<sub>2</sub>-donor Schiff base) and reactions with trimethylaluminum to form cationic aluminum species  
AU Corden, Jonathan P.; Errington, William; Moore, Peter; Wallbridge, Malcolm G. H.  
CS Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK  
SO Chemical Communications (Cambridge) (1999), (4), 323-324  
CODEN: CHCOFS; ISSN: 1359-7345  
PB Royal Society of Chemistry  
DT Journal  
LA English  
AB The 1st example of a cis-configuration of the TiCl<sub>2</sub> group in a six-coordinate titanium complex [(L)TiCl<sub>2</sub>], involving a tetradentate N<sub>2</sub>O<sub>2</sub>-donor Schiff base ligand (L<sub>2</sub>-), is reported. These complexes act as catalysts for the polymerization of ethene in the presence of MAO. The β-cis configuration of the complex [(L)TiCl<sub>2</sub>] (3, H<sub>2</sub>L is the Schiff base from the 1:2 condensation of trans-cyclohexane-1,2-diamine with 2-propionylphenol) was determined by x-ray crystallog. (3·CHCl<sub>3</sub>: monoclinic, space group P2<sub>1</sub>/c, R<sub>1</sub> = 0.053). The reaction of the complex trans-[(L)TiCl<sub>2</sub>] (H<sub>2</sub>L is the Schiff base from the 1:2 condensation of ethane-1,2-diamine with 2-propionylphenol) with trimethylaluminum generated first the complex [(L)TiCl<sub>2</sub>]·2AlMe<sub>3</sub>, and then [(L)(AlMe)(AlMe<sub>2</sub>)]+[AlCl<sub>3</sub>Me]<sup>-</sup>, which crystallized in the orthorhombic space group Pna2<sub>1</sub>, R<sub>1</sub> = 0.074.

RE.CNT 17 THERE ARE 17 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 22 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
AN 1998:605762 CAPLUS  
DN 129:316365  
TI Bis(boryl)metallocenes. 2. Syntheses of 1,1'-Bis(boryl)cobaltocenium Complexes  
AU Herberich, Gerhard E.; Englert, Ulli; Fischer, Andreas; Wiebelhaus, Dag  
CS Institut fuer Anorganische Chemie, Technische Hochschule Aachen, Aachen, D-52056, Germany  
SO Organometallics (1998), 17(22), 4769-4775  
CODEN: ORGND7; ISSN: 0276-7333  
PB American Chemical Society  
DT Journal  
LA English  
OS CASREACT 129:316365  
AB Bis(boryl)cobaltocenes Co(C<sub>5</sub>H<sub>4</sub>BR<sub>2</sub>)<sub>2</sub> (1) can be made from CoBr<sub>2</sub>(DME) and alkali metal borylcyclopentadienides M(C<sub>5</sub>H<sub>4</sub>BR<sub>2</sub>) (M = Li, Na) (2). The two dialkylamino compds. 1c (R = NMe<sub>2</sub>) and 1d (R = NEt<sub>2</sub>) can be obtained in this way. Oxidation with C<sub>2</sub>Cl<sub>6</sub> provides the ionic cobaltocenium chlorides (1c)Cl and (1d)Cl. Further cobaltocenium compds. can be synthesized by modification of the substituents at B. Treatment of (1d)Cl with excess

BCl<sub>3</sub> affords the highly reactive chloride Co(C<sub>5</sub>H<sub>4</sub>BCl<sub>2</sub>)(C<sub>5</sub>H<sub>4</sub>BCl<sub>3</sub>) (5). Pinacolysis of 5 then affords the monosubstitution product Co[C<sub>5</sub>H<sub>4</sub>B(OCMe<sub>2</sub>)<sub>2</sub>](C<sub>5</sub>H<sub>4</sub>BCl<sub>3</sub>) (9) and the disubstitution product [Co{C<sub>5</sub>H<sub>4</sub>B(OCMe<sub>2</sub>)<sub>2</sub>}<sub>2</sub>]Cl [(1h)Cl], resp., depending on stoichiometry and reaction conditions. Reaction of 5 with tetramethyltin replaces two Cl atoms with Me groups to give Co(C<sub>5</sub>H<sub>4</sub>BMe<sub>2</sub>)(C<sub>5</sub>H<sub>4</sub>BCl<sub>3</sub>) (10), while the more reactive trimethylaluminum replaces four Cl substituents to give [Co(C<sub>5</sub>H<sub>4</sub>BMe<sub>2</sub>)<sub>2</sub>]AlCl<sub>4</sub> [(1b)AlCl<sub>4</sub>] and, after metathesis with NBu<sub>4</sub>PF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>, the more convenient hexafluorophosphate (1b)PF<sub>6</sub>. The corresponding cobaltocene 1b is then accessible via conventional amalgam reduction of (1b)AlCl<sub>4</sub>. Reaction of 5 with com. AsF<sub>3</sub> affords the robust inverse chelate Co(C<sub>5</sub>H<sub>4</sub>BF<sub>2</sub>)<sub>2</sub>(μ-OH) (11). Three structural types are encountered for the cobaltocenium derivs.: (i) ionic compds. (type A) such as (1c,d,h)Cl, (1b)AlCl<sub>4</sub>, and (1b)PF<sub>6</sub>; (ii) zwitterionic or semiquaternized compds. (type B) with one trigonal and one tetrahedral B center such as 5, 9, and 10; of these, 5 is fluxional in solution with two effectively equivalent ligands while 9 and 10 display static structures; and (iii) the inverse chelate structure of 11 (type C) which is found in the crystal and in solution. The crystal and mol. structures of 11 were determined

by

x-ray crystallog.

RE.CNT 22 THERE ARE 22 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 23 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1998:172335 CAPLUS

DN 128:252058

TI Some crown ether chemistry of Ti, Zr and Hf derived from liquid clathrate media

AU Alvanipour, Abbas; Atwood, Jerry L.; Bott, Simon G.; Junk, Peter C.; Kynast, Ulrich H.; Prinz, Horst

CS Department of Chemistry, University of Missouri-Columbia, Columbia, MO, 65211, USA

SO Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1998), (7), 1223-1228

CODEN: JCDBTBI; ISSN: 0300-9246

PB Royal Society of Chemistry

DT Journal

LA English

AB The reaction of [Ti(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>] with HCl(g) in the presence of 18-crown-6 formed the oxonium ion-containing complex [H<sub>3</sub>O<sup>+</sup>·18-crown-6][TiCl<sub>5</sub>(H<sub>2</sub>O)-] (1). Its crystal structure shows the oxonium ion resides within the crown ether and has a pyramidal structure. Treatment of [Ti(η-C<sub>5</sub>H<sub>5</sub>)Cl<sub>3</sub>] with AlMe<sub>3</sub> in the presence of 18-crown-6 gave the titanium(III) complex [Ti(η-C<sub>5</sub>H<sub>5</sub>)Cl·18-crown-6][AlCl<sub>2</sub>Me<sub>2</sub>] (2). The structure of 2 reveals a cation with a five-coordinate Ti where the centroid of the C<sub>5</sub>H<sub>5</sub> ring occupies the apex of a square pyramid. The crown ether 18-crown-6 underwent C-O bond scission by treatment with ZrCl<sub>4</sub> in the presence of THF to form the ring-opened zirconium(IV) coordination complex [ZrCl<sub>2</sub>·(OCH<sub>2</sub>CH<sub>2</sub>)<sub>5</sub>OCH<sub>2</sub>CH<sub>2</sub>Cl<sup>+</sup>][ZrCl<sub>5</sub>(THF)-] (3). The structure of 3 shows the formation of a zirconium alkoxide species formed by the ring-opening reaction. The seven-coordinate zirconium center has pentagonal-bipyramidal geometry with two chloride atoms in the axial positions. In an analogous reaction, but in the presence of NaCl, HfCl<sub>4</sub> formed the ionic complex [Na<sup>+</sup>·18-crown-6][HfCl<sub>5</sub>(THF)-] (4), which has a structure similar to that of (1). 1-4 Were characterized by x-ray crystallog. (1: monoclinic, space group P2<sub>1</sub>/c, R = 0.049; 2: monoclinic, space group P2<sub>1</sub>/c, R = 0.070; 3: triclinic, space group P.hivin.1, R = 0.068; 4: monoclinic, space group P2<sub>1</sub>/c, R = 0.049).

RE.CNT 42 THERE ARE 42 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 24 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1997:259744 CAPLUS  
 DN 126:277519  
 TI Base Effects on the Formation of Four- and Five-Coordinate Cationic Aluminum Complexes  
 AU Jegier, Jolin A.; Atwood, David A.  
 CS Department of Chemistry Center for Main Group Chemistry, North Dakota State University, Fargo, ND, 58105, USA  
 SO Inorganic Chemistry (1997), 36(10), 2034-2039  
 CODEN: INOCAJ; ISSN: 0020-1669  
 PB American Chemical Society  
 DT Journal  
 LA English  
 AB This work was conducted as part of the authors' continuing effort to determine the factors that affect cation formation for organometallic Al complexes. The interactions of  $R_2AlX$  ( $R = Me, iBu, tBu$ ;  $X = Cl, Br, iodo$ ) with the monodentate bases THF, pyridine,  $NEt_3$ ,  $HNiPr_2$ ,  $H_2NiBu$ ,  $H_2NtBu$ , and  $O:PPh_3$  were examined to determine the role of the base in cation formation. These reactions resulted in the 9 neutral adducts  $R_2AlX \cdot base$  as well as the 3 cationic complexes  $[R_2Al(base)_2]X$ . The reactions of  $Me_2AlX$  ( $X = Cl, Br$ ) with PMDETA ( $N,N',N'',N'''$ -pentamethyldiethylenetriamine) and the catalytic activity of the resulting 2 cationic complexes are also discussed. All of the compds. were characterized by m.p., IR,  $^1H$ -NMR, and elemental analyses, and in one an x-ray crystallog. study was carried out. X-ray data for  $[(PMDETA)AlMe_2][Me_2AlCl_2]$  (13): triclinic, space group  $P_{21}2_12_1$ ,  $a$  6.9542(6),  $b$  12.2058(10),  $c$  13.2417(11) Å,  $\alpha$  106.236(2),  $\beta$  98.885(2),  $\gamma$  93.807(2)°, and  $Z = 2$  for 181 parameters refined on 4358 reflections having  $F > 6.0\sigma(F)$ ,  $R = 0.0697$ , and  $R_w = 0.0697$ . Complex 13 showed some activity as catalyst in living polymerization of propylene oxide, affording the corresponding oligoether.

L4 ANSWER 25 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1996:592441 CAPLUS  
 DN 125:301142  
 TI Formation of titanium-aluminum Schiff base complexes: x-ray structure of  $[Ti(\mu-Cl)(AlMe_2)(\mu-Cl)(AlMe_2X)(salen)]$  ( $X = Me$  or  $Cl$ )  
 AU Kelly, David G.; Toner, Andrew J.; Walker, Neil M.; Coles, Simon J.; Hursthouse, Michael B.  
 CS Dep. Chem., Manchester Metropolitan Univ., Manchester, M1 5GD, UK  
 SO Polyhedron (1996), 15(23), 4307-4310  
 CODEN: PLYHDE; ISSN: 0277-5387  
 PB Elsevier  
 DT Journal  
 LA English  
 AB Reaction of  $[TiCl_2(salen)]$  [ $salen = N,N'$ -ethylenebis(salicylideneimine)] with  $AlMe_3$  in toluene/hexane afforded the hetero-bimetallic  $[Ti\{\mu-Cl\}(AlMe_2)\{\mu-Cl\}(AlMe_2X)\{salen\}]$  ( $X = Me$  or  $Cl$ ), 1 and  $[TiMe\{\mu-Cl\}(AlCl_2Me)\{salen\}]$ , 2; the crystal structure of the titanium(III) complex (1) has been determined. In THF 2 forms the stable monoalkylated titanium(IV) complex  $[Ti(Me)Cl(salen)]$  (3).

L4 ANSWER 26 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1995:308917 CAPLUS  
 DN 122:132352  
 TI Why Do Catalytic Quantities of Lewis Acid Generally Yield More Product than 1.1 Equivalent in the Intramolecular Diels-Alder Reaction with a Furan Diene? Competitive Complexation NMR Studies Provide an Answer  
 AU Hunt, Ian R.; Rogers, Christine; Woo, Simon; Rauk, Arvi; Keay, Brian A.  
 CS Department of Chemistry, University of Calgary, Calgary, AB, T2N 1N4, Can.  
 SO Journal of the American Chemical Society (1995), 117(3), 1049-56  
 CODEN: JACSAT; ISSN: 0002-7863

PB American Chemical Society  
 DT Journal  
 LA English  
 AB The results presented here provide exptl. support for a hypothesis made by us to rationalize literature observations on intramol. Diels-Alder reactions (IMDA) and our own observations on IMDA with a furan diene (IMDAF) regarding the quantity (catalytic or stoichiometric) of Lewis acid required to facilitate reaction. Evidence suggests that the reactions can be divided into two classes: those that proceed with catalytic quantities of Lewis acid (herein defined as type A) and those that require a stoichiometric quantity of Lewis acid (type B). We believe that the relative basicity of the controlling functional groups in addend and adduct can be critical in determining the quantity of Lewis acid required. The relative Lewis basicity has been studied using competitive complexation studies using low-temperature NMR expts. to study the coordination of methylaluminum dichloride (MAC) and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  with model oxygen Lewis bases and IMDAF addends and adducts.

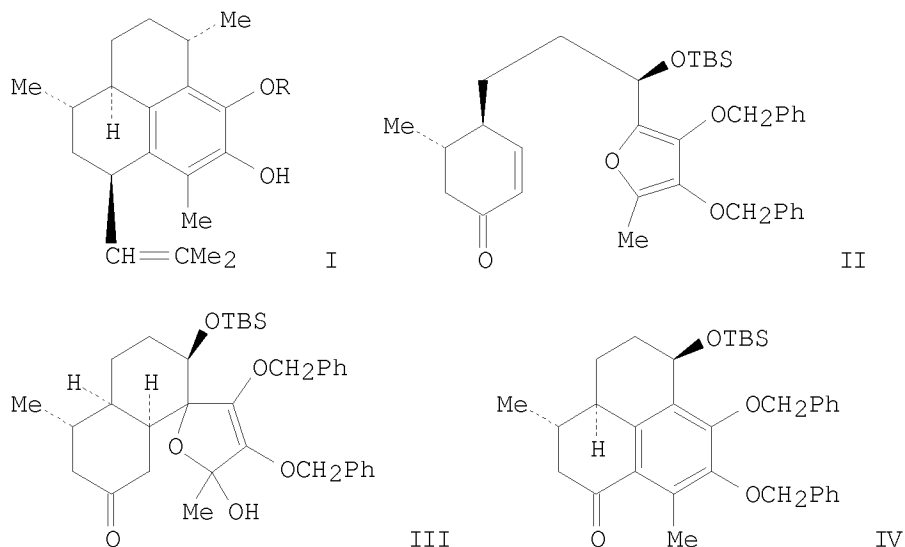
L4 ANSWER 27 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1994:680695 CAPLUS  
 DN 121:280695  
 TI Cationic, Neutral, and Anionic Organoaluminum Species in  $[\text{AlMe}_2(18\text{-crown-6})\text{AlMe}_2\text{X}][\text{AlMe}_3\text{X}]$  ( $\text{X} = \text{Cl}, \text{I}$ )  
 AU Atwood, Jerry L.; Bott, Simon G.; Harvey, Stephen; Junk, Peter C.  
 CS Department of Chemistry, University of Missouri-Columbia, Columbia, MO, 65211, USA  
 SO Organometallics (1994), 13(11), 4151-2  
 CODEN: ORGN7; ISSN: 0276-7333  
 DT Journal  
 LA English  
 AB 18-Crown-6 reacts with  $\text{AlX}_3$  ( $\text{X} = \text{Cl}, \text{I}$ ) in an excess of  $\text{AlMe}_3$  in toluene to form the liquid clathrate species  $[\text{AlMe}_2(18\text{-crown-6})\text{AlMe}_2\text{X}][\text{AlMe}_3\text{X}]$ . The  $\text{AlMe}_2^+$  ion is coordinated to the interior of the macrocycle, while the neutral species is coordinated to the exterior, via an inverted crown O atom.

L4 ANSWER 28 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1994:298773 CAPLUS  
 DN 120:298773  
 TI Synthesis and properties of bis(dichloromethylaluminum)dichlorodiethyllead complex  
 AU Jaworski, Krzysztof  
 CS Inst. Chem., Warsaw Tech. Univ., Plock, 09-400, Pol.  
 SO Bulletin of the Polish Academy of Sciences, Chemistry (1992), 40(4), 287-91  
 CODEN: BPACEQ; ISSN: 0239-7285  
 DT Journal  
 LA English  
 AB  $[\text{Pb}(\text{C}_2\text{H}_5)_2\text{Cl}_2.(\text{AlCH}_3\text{Cl}_2)_2]$  containing different alkyl groups attached to the lead and aluminum atoms was prepared by heating the components in benzene. The complex appeared to be an active catalyst in the redistribution reaction of alkyl groups between  $\text{Pb}(\text{CH}_3)_4$  and  $\text{Pb}(\text{C}_2\text{H}_5)_4$ .

L4 ANSWER 29 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1993:428385 CAPLUS  
 DN 119:28385  
 TI Efficient synthesis of a hexasubstituted aromatic ring via an intramolecular Michael-aldol process: preparation of a late tricyclic intermediate for the synthesis of pseudopterosin A  
 AU Jung, Michael E.; Siedem, Christopher S.  
 CS Dep. Chem. Biochem., Univ. California, Los Angeles, CA, 90024, USA  
 SO Journal of the American Chemical Society (1993), 115(9), 3822-3



DT Journal  
 LA English  
 OS CASREACT 119:28385  
 GI



AB An efficient synthesis of a trisubstituted phenalene derivative containing the tricyclic ring skeleton of pseudopterosin A (I; R =  $\beta$ -D-xylopyranosyl) is described. The key step involves a novel intramolecular Michael addition of an electron-rich furan in II (TBS = SiMe<sub>2</sub>CMe<sub>3</sub>) to a cyclohexenone followed by an aldol reaction of III to give IV in good yield.

L4 ANSWER 30 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1992:194493 CAPLUS

DN 116:194493

TI Unprecedented coordination of a silicon-chlorine bond to a transition metal: synthesis and structure of [rac-C<sub>2</sub>H<sub>4</sub>(indenyl)<sub>2</sub>Zr{CH(SiMe<sub>2</sub>Cl)(SiMe<sub>3</sub>)}}][Al<sub>2</sub>Cl<sub>6</sub>.5Me<sub>0.5</sub>] formed by reversible silicon-carbon bond activation

AU Horton, Andrew D.; Orpen, A. Guy

CS Koninklijke/Shell-Lab., Amsterdam, 1003 AA, Neth.

SO Organometallics (1992), 11(3), 1193-201

CODEN: ORGND7; ISSN: 0276-7333

DT Journal

LA English

AB Reaction of Cp'<sub>2</sub>Zr{CH(SiMe<sub>3</sub>)<sub>2</sub>}Cl with a 2-fold excess of AlCl<sub>3</sub> affords the novel Si-C bond activation products [cyclic] [Cp'<sub>2</sub>Zr{CH(SiMe<sub>2</sub>Cl)(SiMe<sub>3</sub>)}}][Al<sub>2</sub>Cl<sub>n</sub>Me<sub>7-n</sub>] [Cp'<sub>2</sub> = rac-C<sub>2</sub>H<sub>4</sub>(indenyl)<sub>2</sub> (1), (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]; the Lewis acid adducts Cp'<sub>2</sub>Zr{CH(SiMe<sub>3</sub>)<sub>2</sub>}Cl·AlCl<sub>3</sub> are obtained with 1 equivalent of AlCl<sub>3</sub>. In contrast, Cp'<sub>2</sub>Zr(CH<sub>2</sub>SiMe<sub>3</sub>)Cl (Cp'<sub>2</sub> = rac-C<sub>2</sub>H<sub>4</sub>(indenyl)<sub>2</sub>, (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>) undergoes rapid alkyl-chloride exchange with AlCl<sub>3</sub>, giving Cp'<sub>2</sub>ZrCl<sub>2</sub>·Me<sub>3</sub>SiCH<sub>2</sub>AlCl<sub>2</sub>. The structure of 1 was determined by x-ray crystallog. The unusual chelating alkyl ligand shows the first example of Si-Cl bond coordination to a transition metal. The Si-C bond activation reaction leading to 1 is reversible, as shown by formation of rac-C<sub>2</sub>H<sub>4</sub>(indenyl)<sub>2</sub>Zr{CH(SiMe<sub>3</sub>)<sub>2</sub>}Cl on reaction of 1 with a 2-fold excess of AlMe<sub>3</sub>. Sterically and electronically saturated 1 is inert toward unsatd. substrates. Treatment of 1 with Lewis bases affords rac-C<sub>2</sub>H<sub>4</sub>(indenyl)<sub>2</sub>Zr{η<sup>1</sup>-CH(SiMe<sub>2</sub>Cl)(SiMe<sub>3</sub>)}Cl.

L4 ANSWER 31 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1990:572115 CAPLUS  
 DN 113:172115  
 TI Reaction of trimethylaluminum with selenium tetrachloride: synthesis of  
 [(CH<sub>3</sub>)<sub>3</sub>Se][ClAl(CH<sub>3</sub>)<sub>2</sub>(Cl)Al(CH<sub>3</sub>)<sub>3</sub>], the first selenium-based liquid  
 clathrate  
 AU Sangokoya, Samuel A.; Robinson, Gregory H.  
 CS Dep. Chem., Clemson Univ., Clemson, SC, 29634-1905, USA  
 SO Journal of Inclusion Phenomena and Molecular Recognition in Chemistry ( 1990), 9(1), 85-8  
 CODEN: JIMCEN; ISSN: 0923-0750  
 DT Journal  
 LA English  
 AB SeCl<sub>4</sub> reacts with an excess of Me<sub>3</sub>Al in the presence of aromatic solvents to afford a nonstoichiometric organoaluminum-selenonium based inclusion compound [Me<sub>3</sub>Se][ClAlMe<sub>2</sub>(Cl)AlMe<sub>3</sub>](aromatic solvent)<sub>n</sub>. The cation of the parent compound of the inclusion complex results from the alkylation of SeCl<sub>4</sub> producing the Me<sub>3</sub>Se<sup>+</sup> selenonium ion while the anion consists of a Me<sub>2</sub>AlCl unit and a Me<sub>3</sub>Al unit bridged by a chlorine atom. This liquid inclusion complex, a liquid clathrate, can accommodate 8.5 benzene mols. or 8.3 guest toluene mols. per anionic moiety.

L4 ANSWER 32 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1990:406414 CAPLUS  
 DN 113:6414  
 TI Synthesis and molecular structure of {[Se(CH<sub>3</sub>)<sub>3</sub>][(CH<sub>3</sub>)AlCl<sub>3</sub>]}<sub>n</sub>: a novel two-dimensional layered organoaluminum-selenium polymer  
 AU Sangokoya, Samuel A.; Pennington, William T.; Robinson, Gregory H.  
 CS Dep. Chem., Clemson Univ., Clemson, SC, 29634-1905, USA  
 SO Journal of Crystallographic and Spectroscopic Research (1990), 20(1), 53-7  
 CODEN: JCREDB; ISSN: 0277-8068  
 DT Journal  
 LA English  
 AB The crystalline product [(SeMe<sub>3</sub>)(MeAlCl<sub>3</sub>)]<sub>n</sub> (I) was prepared from reaction of SeCl<sub>4</sub> with Me<sub>3</sub>Al in heptane and its x-ray crystal structure was determined. The asym. unit contains one selenonium ion, SeMe<sub>3</sub><sup>+</sup>, and one organoaluminum anionic species MeAlCl<sub>3</sub><sup>-</sup>. Secondary interactions (Se...Cl) link the ions along two dimensions to form infinite layers to give I as a layered organoaluminum-selenium polymer. The mean Se-C bond distance is 1.921(5) Å while the mean C-Se-C bond angle is 9.14(4)°. The independent Al-C bond distance is 1.927 Å while the mean Al-Cl bond distance is 1.166(7) Å.

L4 ANSWER 33 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1990:118894 CAPLUS  
 DN 112:118894  
 TI Alkylation of tellurium tetrachloride by trimethylaluminum: synthesis and molecular structure of [Te(CH<sub>3</sub>)<sub>3</sub>][Al(CH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]: a novel organotelluronium-aluminum oligomer  
 AU Sangokoya, Samuel A.; Pennington, William T.; Robinson, Gregory H.  
 CS Dep. Chem., Clemson Univ., Clemson, SC, 29634-1905, USA  
 SO Journal of Crystallographic and Spectroscopic Research (1989), 19(3), 433-8  
 CODEN: JCREDB; ISSN: 0277-8068  
 DT Journal  
 LA English  
 AB Reaction of TeCl<sub>4</sub> with AlMe<sub>3</sub> in toluene affords [TeMe<sub>3</sub>][AlMe<sub>2</sub>Cl<sub>2</sub>] for which an x-ray crystal structure was determined. The compound does not exist as discrete cations and anions but may be described as an organotelluronium-aluminum oligomer. The mean Te-C bond distance is

2.130(11) Å while the mean Al-Cl bond distance is 2.221(4) Å.

- L4 ANSWER 34 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
AN 1989:646694 CAPLUS  
DN 111:246694  
TI Reaction of organoaluminum species with bidentate phosphine ligands. Synthesis and molecular structure of  $[\text{AlCl}_3][(\text{Ph}_2\text{P})_2\text{CH}_2][\text{AlCl}_2(\text{CH}_3)]$  and  $[\text{AlCl}_3]_2[(\text{Ph}_2\text{P}(\text{O}))_2\text{CH}_2]$   
AU Sangokoya, Samuel A.; Lee, Baosheng; Self, Mark F.; Pennington, William T.; Robinson, Gregory H.  
CS Dep. Chem., Clemson Univ., Clemson, SC, 29634-1905, USA  
SO Polyhedron (1989), 8(12), 1497-1502  
CODEN: PLYHDE; ISSN: 0277-5387  
DT Journal  
LA English  
AB Reaction of  $\text{Me}_3\text{Al}_2\text{Cl}_3$  with  $(\text{Ph}_2\text{P})_2\text{CH}_2$  and  $(\text{Ph}_2\text{P}(\text{O}))_2\text{CH}_2$  affords  $[\text{AlCl}_3][\mu-(\text{Ph}_2\text{P})_2\text{CH}_2][\text{AlCl}_2(\text{Me})]$  (I) and  $[\text{AlCl}_3]_2[(\text{Ph}_2\text{P}(\text{O}))_2\text{CH}_2]$  (II), resp. I crystallizes in triclinic space group  $P_{\bar{1}}$ ,  $a$  10.009(3),  $b$  10.748(4),  $c$  14.806(5) Å,  $\alpha$  90.38(3),  $\beta$  103.36(2),  $\gamma$  96.89(3)°,  $Z = 2$ ,  $R = 0.047$ ,  $R_w = 0.066$ . II crystallizes in monoclinic space group  $C_2$ ,  $a$  12.773(2),  $b$  13.028(3),  $c$  9.461(2) Å,  $\beta$  104.43(2)°,  $Z = 2$ ,  $R = 0.043$ ,  $R_w = 0.050$ . Both products result from reaction of the redistribution products of  $\text{Me}_3\text{Al}_2\text{Cl}_3$ ,  $\text{AlCl}_3$  and  $\text{AlCl}_2\text{Me}$ .
- L4 ANSWER 35 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
AN 1989:75597 CAPLUS  
DN 110:75597  
TI Alternative methods of modifying the calixarene conformation. The synthesis and molecular structures of tert-butylcalix[4]arene methyl ether complexes with aluminum alkyl species  
AU Bott, Simon G.; Coleman, Anthony W.; Atwood, Jerry L.  
CS Dep. Chem., Univ. Alabama, Tuscaloosa, AL, 35487, USA  
SO Journal of Inclusion Phenomena (1987), 5(6), 747-58  
CODEN: JOIPDF; ISSN: 0167-7861  
DT Journal  
LA English  
AB The mol. structures of the title complexes were confirmed by x-ray crystallog. and NMR analyses. The configurations of calix[4]arenes may be modified by the formation of donor-acceptor complexes which make use of the oxygen atoms of the macrocycle. Thus, [tert-butylcalix[4]arene Me ether] $[\text{AlMe}_3]_2$  exhibits the previously unseen 1,2-alternate geometry, while [tert-butylcalix[4]arene Me ether] $[\text{MeAlCl}_2]_2$  and [tert-butylcalix[4]arene Me ether] $[\text{EtAlCl}_2]_2$  show the 1,3-alternate configuration. The Al-O lengths in all three complexes are normal for donor-acceptor interactions.
- L4 ANSWER 36 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
AN 1988:611116 CAPLUS  
DN 109:211116  
TI Sterically crowded aryloxide compounds of aluminum  
AU Healy, Matthew D.; Wierda, Derk A.; Barron, Andrew R.  
CS Dep. Chem., Harvard Univ., Cambridge, MA, 02138, USA  
SO Organometallics (1988), 7(12), 2543-8  
CODEN: ORGND7; ISSN: 0276-7333  
DT Journal  
LA English  
OS CASREACT 109:211116  
AB Reaction of  $\text{AlMe}_3$  with 2 equiv of the sterically hindered phenol 2,6-di-tert-butyl-4-methylphenol (BHT-H) gives the disubstituted compound  $\text{AlMe}(\text{BHT})_2$  (I), whereas excess of  $\text{AlMe}_3$  leads to the compound  $\text{AlMe}_2(\text{BHT})_2$  (II). Addition of  $\text{PMe}_3$  to I and II yields  $\text{AlMe}(\text{BHT})_2(\text{PMe}_3)$  and

AlMe<sub>2</sub>(BHT)(PMe<sub>3</sub>) (III), resp. The addition of 1 equiv of Me<sub>3</sub>NHCl to I and III gave AlCl(BHT)<sub>2</sub>(NMe<sub>3</sub>) and AlClMe(BHT)(NMe<sub>3</sub>) (IV); reaction of a further equivalent of Me<sub>3</sub>NHCl to IV affords the ionic complex [Me<sub>3</sub>NH][AlMeCl<sub>2</sub>(BHT)] (V). The mol. structures of III and V were determined by x-ray crystallog. The Al-O distances are shorter and Al-O-C angles larger than usually found for aluminum alkoxides. The possibility of a  $\pi$ -type interaction between Al and O is discussed.

L4 ANSWER 37 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1988:197093 CAPLUS

DN 108:197093

TI Aluminum dichloride and dibromide. Preparation, spectroscopic (including matrix isolation) study, reactions, and role (together with alkyl(aryl)aluminum monohalides) in the preparation of organoaluminum compounds

AU Olah, George A.; Farooq, Omar; Farnia, S. Morteza F.; Bruce, Mark R.; Clouet, Francoise L.; Morton, Peter R.; Prakash, G. K. Surya; Stevens, Raymond C.; Bau, Robert; et al.

CS Donald P. and Katherine B. Loker Hydrocarbon Res. Inst., Univ. Southern California, Los Angeles, CA, 90089-1661, USA

SO Journal of the American Chemical Society (1988), 110(10), 3231-8  
CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

OS CASREACT 108:197093

AB Anhydrous AlX (X = Cl, Br) when heated in a 2:1 molar ratio with Al powder in a suspension of dry heptane or methylcyclohexane is partially reduced to AlX<sub>2</sub>. Ultrasound treatment (sonication) significantly promotes the reaction. AlCl<sub>2</sub> in higher purity was obtained by the reaction of gaseous AlCl<sub>3</sub> with Al-metal in a high-vacuum reactor, allowing subsequent study by IR spectroscopy. AlCl<sub>2</sub> in higher purity was also obtained by the high-temperature reaction of gaseous AlCP<sub>3</sub> with Al-metal in a high-vacuum reactor. Al<sub>2</sub>(iso-Bu)<sub>4</sub>-xCl<sub>x</sub> was also prepared through the reaction of Al<sub>2</sub>(iso-Bu)<sub>4</sub> and HCl at low temperature. Both materials were studied by IR spectroscopy and compared to AlCl<sub>2</sub> prepared and isolated through the codeposition of Al atoms and Cl<sub>2</sub> in a solid Ar matrix. The matrix study characterized AlCl<sub>2</sub> together with AlCl and AlCl<sub>3</sub>, which were also formed in the system. Paramagnetic AlX<sub>2</sub> are associated in the condensed state (except under matrix isolation conditions where they are monomeric). An ESR study of the pyridinium complex of AlCl<sub>2</sub> was carried out and showed its paramagnetic nature. In the present study, for simplicity, the reactions of AlX<sub>2</sub> are considered as those of the dimers but could involve higher associated oligomers. MNDO calcns. on the heats of formation of 7 possible isomeric structures of Al<sub>2</sub>Cl<sub>4</sub> indicate the preference for both halogen bridging and significant Al-Al bonding in the dimer. Reaction of AlCl<sub>3</sub> + Al with CH<sub>2</sub>H<sub>4</sub>, the Hall and Nash reaction, was restudied by <sup>13</sup>C and <sup>27</sup>Al NMR spectroscopy. The reaction gives, besides Al<sub>2</sub>EtCl<sub>3</sub>, 1,2- and 1,1-C<sub>2</sub>H<sub>4</sub>(AlCl<sub>2</sub>)<sub>2</sub>. Cyclohexene in a similar reaction gives, although less readily, 1,2-bis(dichloroaluminio)cyclohexane. The reactions are indicative of addition of (AlCl<sub>2</sub>)<sub>2</sub> to the olefins. Alkyl- and arylaluminum monohalides are intermediately formed in the reaction of alkyl halides or halobenzenes with active Al powder. AlX<sub>2</sub> are also considered to be dimeric in nature and immediately react with excess of the alkyl (aryl) halides to form the corresponding sesquihalides. AlX<sub>2</sub> formed in the AlX<sub>3</sub>-Al metal systems react with alkyl or aryl halides to give alkyl(aryl)aluminum dihalides. Sonication was found to significantly promote these reactions.

L4 ANSWER 38 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1988:15200 CAPLUS

DN 108:15200

TI Preparation and structure of the dichloro[15-crown-5]ytterbium(1+) cation,

an example of seven-coordinate ytterbium

AU Atwood, David A.; Bott, Simon G.; Atwood, Jerry L.  
 CS Dep. Chem., Univ. Alabama, University, AL, 35486, USA  
 SO Journal of Coordination Chemistry (1987), 16(1), 93-6  
 CODEN: JCCMBQ; ISSN: 0095-8972

DT Journal  
 LA English

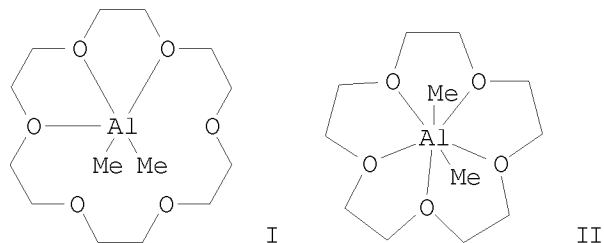
AB [YbCl<sub>2</sub>(15-crown-5)][AlCl<sub>2</sub>Me<sub>2</sub>] was prepared by the reaction of YbCl<sub>3</sub>, 15-crown-5, and AlMe<sub>3</sub> (1:1:4) in toluene. The colorless air-sensitive crystals belong to the orthorhombic space group Pmma with a 11.313(7), b 10.907(5), c 17.716(7) Å, and d.(calculated) = 1.81 g cm<sup>-3</sup>, Z = 4, R = 0.048 based on 1502 observed reflection. The Yb atom is displaced 0.20 Å from the plane of the crown ether, and the Yb-O bond distance are 2.23-2.32 Å.

L4 ANSWER 39 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1987:407248 CAPLUS  
 DN 107:7248  
 OREF 107:1339a,1342a

TI Stabilization of cations [AlMe<sub>2</sub>]<sup>+</sup> with crown ethers

AU Bott, Simon G.; Alvanipour, Abbas; Morley, S. David; Atwood, David A.; Means, C. Mitchell; Coleman, Anthony W.; Atwood, Jerry L.  
 CS Dep. Chem., Univ. Alabama, Tuscaloosa, AL, 35487, USA  
 SO Angewandte Chemie (1987), 99(5), 476-8  
 CODEN: ANCEAD; ISSN: 0044-8249

DT Journal  
 LA German  
 OS CASREACT 107:7248  
 GI



AB Condensation of 18-crown-6 or 15-crown-5 with Me<sub>3</sub>Al in the presence of titanocene dichloride or CoCl<sub>2</sub> gave crown ether-stabilized Me<sub>2</sub>Al<sup>+</sup> cations I and II. The crystal structures of I and II are reported.

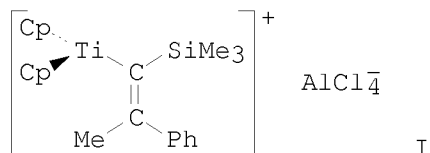
L4 ANSWER 40 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1986:5969 CAPLUS  
 DN 104:5969  
 OREF 104:1095a,1098a

TI Organometallic compounds of Group III. Part 41. Direct observation of the initial insertion of an unsaturated hydrocarbon into the titanium-carbon bond of the soluble Ziegler polymerization catalyst Cp<sub>2</sub>TiCl<sub>2</sub>-MeAlCl<sub>2</sub>

AU Eisch, John J.; Piotrowski, Andrzej M.; Brownstein, Sydney K.; Gabe, Eric J.; Lee, Florence L.  
 CS Dep. Chem., State Univ. New York, Binghamton, NY, 13901, USA  
 SO Journal of the American Chemical Society (1985), 107(24), 7219-21  
 CODEN: JACSAT; ISSN: 0002-7863

DT Journal  
 LA English

OS CASREACT 104:5969  
GI



AB PhC.tplbond.CSiMe3 reacted with Cp2TiCl2 (Cp =  $\eta^5$ -cyclopentadienyl) and MeAlCl2 to give the alkenyl Ti complex I. The x-ray crystal structure of I showed the Ti, Si, vinyl carbons, and the Me and Cl-Ph carbons were essentially planar.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{27}\text{Al}$  NMR spectroscopy showed I was the first and only insertion product formed in this reaction. Cp2TiCl2 and MeAlCl2 gave Cp2TiCl( $\mu$ -Cl)AlCl2Me (II), as confirmed by x-ray crystallog. Cp2TiMe+ AlCl4-, formed by dissociation of II, was proposed as the active catalyst for Ziegler polymn systems.

L4 ANSWER 41 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1985:596144 CAPLUS

DN 103:196144

OREF 103:31613a,31616a

TI Complexes of alkali earth metal halides with alkyl aluminum dihalides

AU Giannini, U.; Albizzati, E.; Zucchini, U.

CS Montedison Group, Ist. G. Donegani S.p.A., Novara, 28100, Italy

SO Inorganica Chimica Acta (1985), 98(3), 191-4

CODEN: ICHAA3; ISSN: 0020-1693

DT Journal

LA English

AB The reaction of MX2 (M = Mg, Ca, Si, Ba; X = Cl, Br, I) with RAlX2 (R = Me, Et, Bu; X = Cl, Br, I) gave 72.4-97.0% MX2.nRAlX2 (n = 1-4).

L4 ANSWER 42 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1985:415936 CAPLUS

DN 103:15936

OREF 103:2527a,2530a

TI Mononuclear and binuclear cationic complexes of vanadium(II)

AU Cotton, F. Albert; Duraj, Stan A.; Manzer, Leo E.; Roth, Wieslaw J.

CS Dep. Chem., Texas A and M Univ., College Station, TX, 77843, USA

SO Journal of the American Chemical Society (1985), 107(13), 3850-5

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

AB A method for the high-yield preparation ( $\leq 99\%$ ) of the new [(THF)3V( $\mu$ -Cl)3V(THF)3]AlCl2R2 (I; R = Et or Me) is described. I (R = Et) reacts instantaneously with MeOH to give a blue solution from which, depending upon the workup, [V(MeOH)6]Cl2 (II) or VC12(MeOH)4 can be obtained. With PMe3, I (R = Et) readily affords [(PMe3)3V( $\mu$ -Cl)3V(PMe3)3]AlCl2Et2 (III). Crystals of I (R = Et) diffracted poorly, and the structure could not be satisfactorily refined because of severe disorder in the THF ligands as well as in [Et2AlCl2]-. The structure was solved, however, and refined sufficiently to define V2(THF)6( $\mu$ -Cl)3+ cation and Et2AlCl2- anion unambiguously but not accurately. Further characterization came from elemental anal. on all 6 elements of I (R = Et) and its UV spectrum. II crystallizes in space group P21/n with a 6.993(3), b 10.809(4), c 10.298(4) Å,  $\beta$  97.00(3)°, Z = 2. II represents the 1st example of a homoleptic V(II) alcoholate to be fully characterized by x-ray crystallog. For III the orthorhombic unit cell

(space group Pnma) has a 12.705(2), b 12.522(4), c 28.554(9) Å, and Z = 4. The V-V' distance (in III) is 3.103(4) Å.

L4 ANSWER 43 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1984:409562 CAPLUS

DN 101:9562

OREF 101:1573a,1576a

TI Purifying aluminum chloride

IN Tkachenko, A. F.; Groshev, G. L.; Bodrikov, I. V.

PA USSR

SO U.S.S.R.

From: Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1984, (13), 63-4.

CODEN: URXXAF

DT Patent

LA Russian

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	SU 1084248	A1	19840407	SU 1982-3409943	19820324 <--
PRAI	SU 1982-3409943		19820324		
AB	The degree of purification of AlCl <sub>3</sub> is increased by using RAlCl <sub>2</sub> (R = Me or Et) as a solvent for recrystn.				

L4 ANSWER 44 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1984:6762 CAPLUS

DN 100:6762

OREF 100:1167a,1170a

TI Studies on tungsten hexacarbonyl and (arene)tungsten tricarbonyl derived catalysts in metathesis of linear olefins. IR and proton NMR investigation on systems: (arene)tungsten tricarbonyl + RAlCl<sub>2</sub> + oxygen (O<sub>2</sub>)

AU Korda, Anna; Giezyński, Roman

CS Fac. Chem., Polytech. Univ., Warsaw, 00662, Pol.

SO Polish Journal of Chemistry (1982), 56(4-5-6), 849-54

CODEN: PJCHDQ; ISSN: 0137-5083

DT Journal

LA English

GI For diagram(s), see printed CA Issue.

AB LW(CO)<sub>3</sub> (L = benzene, mesitylene) form adducts I and II (R = H, Me in each case) with EtAlCl<sub>2</sub>. Similar results were obtained with MeAlCl<sub>2</sub>. Addition of O<sub>2</sub> to I and II facilitates arene dissociation. These results were discussed in terms of the metathesis catalysts formed from LW(CO)<sub>3</sub>, RAlCl<sub>2</sub>, and O<sub>2</sub>. W(CO)<sub>6</sub> did not form an adduct with EtAlCl<sub>2</sub>.

L4 ANSWER 45 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1983:16806 CAPLUS

DN 98:16806

OREF 98:2727a,2730a

TI Multiple metal-carbon bonds. 27. Preparation of tungsten(VI) phenylimido alkyl and alkylidene complexes

AU Pedersen, Steven F.; Schrock, Richard R.

CS Dep. Chem., Massachusetts Inst. Technol., Cambridge, MA, 02139, USA

SO Journal of the American Chemical Society (1982), 104(26), 7483-91

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

AB Phenylimido neopentylidene complexes (PhN)W(CHCMe<sub>3</sub>)L<sub>2</sub>Cl<sub>2</sub> (I; L = PMe<sub>3</sub>, PEt<sub>3</sub>) were prepared by treating (PhN)W(OCMe<sub>3</sub>)<sub>4</sub> with (Me<sub>3</sub>CCH)TaL<sub>2</sub>Cl<sub>3</sub>. [(PhN)W(CHCMe<sub>3</sub>)L<sub>2</sub>R]<sup>+</sup> (R = Cl, Me), (PhN)W(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>L and (PhN)W(CHCMe<sub>3</sub>)(L)Cl<sub>2</sub> were prepared straightforwardly from I. (PhN)WNp<sub>3</sub>Cl

(II; Np = CH<sub>2</sub>CMe<sub>3</sub>) was prepared from (PhN)WCl<sub>4</sub> and NpMgCl, and (PhN)W(CHCMe<sub>3</sub>)Np<sub>2</sub> and CpW(NPh)(CHCMe<sub>3</sub>)Np were prepared from II by  $\alpha$ -H abstractions. II reacts with L.HCl (L = PMe<sub>3</sub>, py) in the presence of excess L to give I, presumably via unobservable (PhN)WNp<sub>2</sub>(L)Cl<sub>2</sub>. (PhN)W(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub>, which can be prepared from (PhN)W(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>Cl and LiCH<sub>2</sub>SiMe<sub>3</sub>, decomps. smoothly in a 1st-order reaction to give (PhN)W(CHSiMe<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> while (PhN)W(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> reacts with L = PMe<sub>3</sub> or PEt<sub>3</sub> to give (PhN)W(CHSiMe<sub>3</sub>)L<sub>2</sub>Cl<sub>2</sub>. The preparation of several miscellaneous phenylimido alkyl complexes such as (PhN)WR<sub>3</sub>Cl (R = Me, Bz), CpW(NPh)Me<sub>3</sub>, (PhN)WR<sub>3</sub>(OCMe<sub>3</sub>) (R = Me, Bz, Np), and the product of [(PhN)W(CHCMe<sub>3</sub>)(PMe<sub>3</sub>)<sub>2</sub>Me][AlMe<sub>2</sub>Cl<sub>2</sub>] decomposition, (PhN)W(CCM<sub>3</sub>)(PMe<sub>3</sub>)<sub>2</sub>Cl(AlMe<sub>2</sub>Cl) is also reported.

L4 ANSWER 46 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1982:544902 CAPLUS

DN 97:144902

OREF 97:24140h,24141a

TI Gas-phase positive-ion chemistry of trimethylboron and trimethylaluminum

AU Kappes, Manfred M.; Uppal, Jack S.; Staley, Ralph H.

CS Dep. Chem., Massachusetts Inst. Technol., Cambridge, MA, 02139, USA

SO Organometallics (1982), 1(10), 1303-7

CODEN: ORGND7; ISSN: 0276-7333

DT Journal

LA English

AB Me<sub>2</sub>B<sup>+</sup> and Me<sub>2</sub>Al<sup>+</sup> are the principal ions produced by electron impact on Me<sub>3</sub>B and Me<sub>3</sub>Al, resp. Study of halide transfer to these cations leads to determination of their halide (Cl<sup>-</sup> and F<sup>-</sup>) affinities. These show .apprx.9 kcal/mol greater stability for Me<sub>2</sub>Al<sup>+</sup> compared to Me<sub>2</sub>B<sup>+</sup>. Me<sub>3</sub>B reacts by Me- transfer with CF<sub>3</sub><sup>+</sup> and CF<sub>2</sub>Cl<sup>+</sup>, but not with CCl<sub>3</sub><sup>+</sup>, Me<sub>2</sub>CH<sup>+</sup> or CHCl<sub>2</sub><sup>+</sup>, establishing a value for the Me--anion affinity of Me<sub>2</sub>B<sup>+</sup>. In a related reaction also involving C-C bond formation, CHCl<sub>2</sub><sup>+</sup> and CFC1<sub>2</sub><sup>+</sup> are alkylated with Me<sub>3</sub>Al to give MeCHCl<sup>+</sup> and MeCFC1<sup>+</sup>, resp. Other thermochem. detns. include the hydride affinity of Me<sub>2</sub>B:CH<sub>2</sub><sup>+</sup>. A variety of mols. (L) condense with Me<sub>2</sub>B<sup>+</sup> to yield 1-ligand complexes, and with Me<sub>2</sub>Al<sup>+</sup> to yield 2-ligand complexes. The relative order of ligand-binding energies for these mols. to both species is determined from the preferred direction of displacement reactions: for Me<sub>2</sub>B(L)<sup>+</sup>, Me<sub>2</sub>S < MeCN < PhOMe < Me<sub>2</sub>O < PhCN < pyridine, and for Me<sub>2</sub>Al(L)<sub>2</sub><sup>+</sup>, Me<sub>3</sub>Al < Me<sub>2</sub>S < PhOMe < Me<sub>2</sub>O < MeCN < Et<sub>2</sub>O = (Me<sub>2</sub>CH)<sub>2</sub>O < PhCN < Me<sub>3</sub>N < pyridine. The relative position of MeCN in these series indicates that Me<sub>2</sub>Al<sup>+</sup> is a relatively softer acid than Me<sub>2</sub>B<sup>+</sup> or Al<sup>+</sup>.

L4 ANSWER 47 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1982:122857 CAPLUS

DN 96:122857

OREF 96:20181a,20184a

TI  $\alpha$ -Hydride elimination: the first observable equilibria between alkylidene complexes and alkylidyne hydride complexes

AU Churchill, Melvyn Rowen; Wasserman, Harvey J.; Turner, Howard W.; Schrock, Richard R.

CS Dep. Chem., State Univ. New York, Buffalo, NY, 14214, USA

SO Journal of the American Chemical Society (1982), 104(6), 1710-16

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

AB (Me<sub>3</sub>CCH:)Ta(dmpe)Cl<sub>3</sub> (dmpe = Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>) is reduced by Na amalgam in the presence of dmpe to give (Me<sub>3</sub>CCH:)Ta(dmpe)<sub>2</sub>Cl (I). The Me<sub>3</sub>CCH: ligand is grossly distorted toward a neopentylidyne-hydride system, as evidenced by the low value for  $\nu$ CH $\alpha$  (2200 cm<sup>-1</sup>) and JCH $\alpha$  (57 Hz). Addition of Me<sub>x</sub>AlCl<sub>3-x</sub> reagents generates Al-stabilized neopentylidyne hydride complexes. The crystal structure of complex (Me<sub>3</sub>CC)TaH(dmpe)<sub>2</sub>(ClAlMe<sub>3</sub>) was determined. The Ta atom has a



pentagonal-bipyramidal coordination geometry, with 2 dmpe ligands and the hydride ligand [Ta-H = 1.80 (5) Å] in the equatorial plane. The neopentylidyne ligand [Ta.tplbond.C = 1.850 (5) Å] and a Cl-AlMe<sub>3</sub> ligand [Ta-Cl = 2.768 (2) Å] occupy the 2 axial sites. Replacing the chloride in I with iodide produces a product which at 200 K is approx. a 9:1 mixture of (Me<sub>3</sub>CC)Ta(H)(dmpe)<sub>2</sub>I and (Me<sub>3</sub>CCH)Ta(dmpe)<sub>2</sub>I. At 335 K it is approx. a 1:1 mixture of the 2, and they interconvert rapidly on the NMR time scale. Replacing the chloride with triflate produces a mixture which contains <50% (Me<sub>3</sub>CCH)Ta(dmpe)<sub>2</sub>(O<sub>3</sub>SCF<sub>3</sub>) at 355 K.

L4 ANSWER 48 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1982:35460 CAPLUS

DN 96:35460

OREF 96:5873a,5876a

TI Synthesis and characterization of tungsten oxo neopentylidene complexes

AU Wengrovius, Jeffrey H.; Schrock, Richard R.

CS Dep. Chem., Massachusetts Inst. Technol., Cambridge, MA, 02139, USA

SO Organometallics (1982), 1(1), 148-55

CODEN: ORGND7; ISSN: 0276-7333

DT Journal

LA English

AB (Me<sub>3</sub>CCH:)Ta(PR<sub>3</sub>)<sub>2</sub>X<sub>3</sub> (X = Cl, Br; R<sub>3</sub> = Me<sub>3</sub>, Et<sub>3</sub>, Me<sub>2</sub>Ph) react with W(O)(OCMe<sub>3</sub>)<sub>4</sub> to give [(Me<sub>3</sub>CO)<sub>4</sub>TaX]<sub>2</sub> and (Me<sub>3</sub>CCH:)W(O)(PR<sub>3</sub>)<sub>2</sub>X<sub>2</sub> (I). The R<sub>3</sub>P ligands in I are trans and the oxo and neopentylidene ligands are cis to one another. Five-coordinate complexes can be prepared by scavenging 1 R<sub>3</sub>P ligand with (PhCN)<sub>2</sub>PdCl<sub>2</sub>. Addition of 1 or 2 equiv AlCl<sub>3</sub> to I (X = Cl, R = Et) (II) in CH<sub>2</sub>Cl<sub>2</sub> yields mono- and dicationic complexes, resp. Adding Me<sub>3</sub>Al to II gave unstable [(Me<sub>3</sub>CCH:)W(O)(Me)(PEt<sub>3</sub>)<sub>2</sub>]+ (Me<sub>2</sub>AlCl<sub>2</sub>)<sup>-</sup>, which on treatment with Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (L) yields (Me<sub>3</sub>CCH:)W(O)(L)(Cl)(Me). Attempts to prepare cationic complexes with BF<sub>4</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup> counterions yielded fluoride complexes. Complexes containing tert-butoxide ligands in place of halides were prepared by several routes. Phosphine-free, unstable [(Me<sub>3</sub>CCH:)W(O)(OCMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and other phosphine-free complexes [e.g., (Me<sub>3</sub>CCH:)W(O)(L)Cl<sub>2</sub> and (Me<sub>3</sub>CCH:)W(O)(S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub>] were also prepared

L4 ANSWER 49 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1981:46816 CAPLUS

DN 94:46816

OREF 94:7625a,7628a

TI Alkylaluminum chloride induced cyclization of unsaturated carbonyl compounds

AU Karras, Michael; Snider, Barry B.

CS Dep. Chem., Princeton Univ., Princeton, NJ, 08544, USA

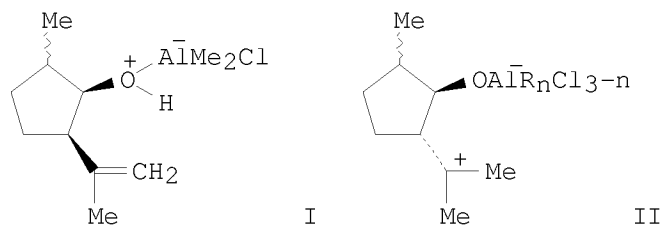
SO Journal of the American Chemical Society (1980), 102(27), 7951-3

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

GI



AB 2,6-Dimethyl-5-heptenal undergoes a concerted ene reaction with 1 equivalent

of Me<sub>2</sub>AlCl at -80° to give I and a cation-olefin cyclization with 2 equivalent of Me<sub>2</sub>AlCl, MeAlCl<sub>2</sub>, or EtAlCl<sub>2</sub> to give a zwitterion II (R = Me, Et; n = 1,2) whose further reactions depend on the Lewis acid used and the temperature 6,7-Unsatd. ketones undergo ene reactions with Me<sub>2</sub>AlCl as catalyst whereas 4,5- and 5,6-unsatd. ketones undergo cation-olefin cyclization with 2 equivalent of MeAlCl<sub>2</sub> to give a zwitterion which undergoes a 1,2-hydride shift, followed by a 1,2-Me shift, to give a cyclopentanone.

L4 ANSWER 50 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1979:23161 CAPLUS

DN 90:23161

OREF 90:3835a,3838a

TI Regiospecific and stereoselective carbometalation of alkynylsilanes by Ziegler-Natta alkylating agents

AU Eisch, John J.; Manfre, Robert J.; Komar, David A.

CS Dep. Chem., State Univ. New York, Binghamton, NY, USA

SO Journal of Organometallic Chemistry (1978), 159(4), C13-C19

CODEN: JORCAI; ISSN: 0022-328X

DT Journal

LA English

OS CASREACT 90:23161

AB A 1:1 combination of dichloro(bis-η<sup>5</sup>-cyclopentadienyl)titanium and alkylaluminum halides in methylene chloride solution effects the regiospecific alkylation of alkynyl(trimethyl)silanes in 60-95% yields. With RC.tplbond.CSiMe<sub>3</sub> substrates, where R = saturated alkyl group, the carbometalation (introduction of a Me or an Et group) occurs regiospecifically and stereoselectively in a trans-manner, giving a 75:25 to a 90:10 ratio of isomers. When the R in RC.tplbond.CSiMe<sub>3</sub> is Ph or 1-cyclohexenyl, then a non-stereoselective carbometalation is observed (50:50 mixts. of isomers). These results, which are explicable in terms of the formation of the (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti+R cation and its attack on the alkynylsilane, offer stereochem. evidence for a cationic initiating step in the polymerization of ethylene by homogeneous Ziegler-Natta catalysts.

L4 ANSWER 51 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1978:105552 CAPLUS

DN 88:105552

OREF 88:16565a,16568a

TI Cuprous organoaluminum and cuprous organoboron complexes and uses thereof

PA Exxon Research and Engineering Co., USA

SO Brit., 9 pp.

CODEN: BRXXAA

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	-----	---	-----	-----	-----
PI	GB 1484775	A	19770908	GB 1975-1067	19750110 <--
PRAI	GB 1975-1067	A	19750110		

AB CuAlRC12R1.nL (I; R = Me, Et, iso-Bu; R1 = Cl, Br; n = 1, 2; L = cyclohexene, 1-pentene, C<sub>6</sub>H<sub>6</sub>) were prepared from CuR1<sub>2</sub> by treatment with RAlCl<sub>2</sub> in L. CH<sub>2</sub>:CH<sub>2</sub> and MeCH:CH<sub>2</sub> were separated from mixts. with C<sub>2</sub>H<sub>6</sub> and propane, resp., by ligand exchange with I. Thus, a mixture of 53 mol % CH<sub>2</sub>:CH<sub>2</sub> and 47 mol % C<sub>2</sub>H<sub>6</sub> was contacted with CuAlEtCl<sub>3</sub>.2C<sub>6</sub>H<sub>6</sub> at 24° and 1 atm; when the solution was saturated, it was heated to 45° under N. The decomplexed product contained 95 mol % CH<sub>2</sub>:CH<sub>2</sub>. Apparatus for the ligand exchange process is described.

L4 ANSWER 52 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1977:535956 CAPLUS

DN 87:135956

OREF 87:21557a,21560a

TI Adducts of  $\pi$ -allyl compounds of transition metals, Lewis bases, and/or Lewis acids

IN Wilke, Guenther

PA Studiengesellschaft Kohle m.b.H., Fed. Rep. Ger.

SO Ger., 10 pp. Division of Ger. 1,520,964.

CODEN: GWXXAW

DT Patent

LA German

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	-----	----	-----	-----	-----
PI	DE 1793788	A1	19741121	DE 1967-1793788	19630810 <--
	DE 1793788	B2	19770113		
	DE 1793788	C3	19770901		
PRAI	DE 1967-1793788	A	19630810		

AB Adducts of  $\pi$ -allylmetal compds. such as LMX (L =  $\pi$ -allyl, M = Cr, Co, Ni, Pd, X = Cl, Br iodo) and L2M, with Al halides such as AlBr3, AlCl3, EtAlCl2, Et2AlCl, and MeAlCl2 catalyzed polymerization and

oligomerization

of alkenes such as ethylene, propylene, butadiene, cyclohexene, and 1-butene. Adducts of  $\pi$ -allylmetal compds., Al halides, and R3P (R = Ph, cyclohexyl, Et, Me2CH, Et2N, o-cresyloxy, PhO, etc.) similarly catalyzed such polymns.

L4 ANSWER 53 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1977:406204 CAPLUS

DN 87:6204

OREF 87:1005a,1008a

TI Organocopper complexes containing aluminum or boron

PA Exxon Research and Engineering Co., USA

SO Jpn. Kokai Tokkyo Koho, 11 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	-----	----	-----	-----	-----
PI	JP 51086425	A	19760729	JP 1975-7652	19750117 <--
	JP 59038208	B	19840914		
PRAI	JP 1975-7652	A	19750117		

AB CuX (X = Cl, Br) and RAlCl2 (R = Me, Et, iso-Bu) were treated at -20° in a solvent Q (Q = C6H6, PhMe, cyclohexene) to give complexes CuAlRC12X.2Q (I, Q as above), which on treating with propylene (II) or a mixture of II and propane at room temperature, gave I (Q = II), which liberated pure II on heating to 100°. Similarly I (Q = ethylene) was prepared.

L4 ANSWER 54 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1976:560218 CAPLUS

DN 85:160218

OREF 85:25657a,25660a

TI Complexes of carbonyl compounds with RnAlX3-n compounds. IV. The evidence for the formation of cyclic complexes with chloroaluminum compounds

AU Starowieyski, K. B.; Pasynkiewicz, S.; Sporzynski, A.

CS Inst. Org. Chem. Technol., Tech. Univ. Warsaw, Warsaw, Pol.

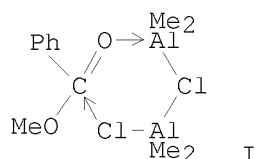
SO Journal of Organometallic Chemistry (1976), 117(2), 117-28

CODEN: JORCAI; ISSN: 0022-328X

DT Journal

LA English

GI



AB Reasonably stable 1:2 complexes (e.g., I) are formed by carbonyl compds. with chloroaluminum compds., usually in equilibrium with a 1:1 complex; however with Me<sub>3</sub>Al only a 1:1 complex is formed. In the case of complexes with an excess of MeAlCl<sub>2</sub>, a disproportionation reaction occurs. Possible structures are discussed in light of PMR and ir spectroscopy, dipole moments and mol. weight determination

L4 ANSWER 55 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1975:479317 CAPLUS

DN 83:79317

OREF 83:12462h,12463a

TI Reactions of methylaluminum compounds with benzyl cyanide

AU Pasykiewicz, Stanislaw; Kuran, Witold; Zbierzchowska, Anna

CS Inst. Org. Chem. Technol., Tech. Univ. Warsaw, Warsaw, Pol.

SO Justus Liebigs Annalen der Chemie (1975), (4), 636-41

CODEN: JLACBF; ISSN: 0075-4617

DT Journal

LA German

OS CASREACT 83:79317

GI For diagram(s), see printed CA Issue.

AB MeAlCl<sub>2</sub> and Me<sub>2</sub>AlCl reacted with PhCH<sub>2</sub>CN via elimination of CH<sub>4</sub> and formation of PhCH<sub>2</sub>C(:NAlCl<sub>2</sub>)CHPhCN and trimer I and II.

PhCH<sub>2</sub>CMe:NAlMen-1Cl<sub>3</sub>-n was formed by rearrangement of PhCH<sub>2</sub>CN.AlMenCl<sub>3</sub>-n (n = 1-3).

L4 ANSWER 56 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1975:410398 CAPLUS

DN 83:10398

OREF 83:1749a,1752a

TI Complex aluminum compounds and alkyl phosphorus halides

IN Coates, Harold; Waring, Derek M. H.

PA United Kingdom Ministry of Supply, UK

SO U.S., 2 pp.

CODEN: USXXAM

DT Patent

LA English

FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 3840576	A	19741008	US 1952-303431	19520808 <--
	GB 1344051	A	19740116	GB 1951-18813	19510809 <--
PRAI	GB 1951-18813	A	19510809		

AB The reaction of MeAlCl<sub>2</sub> with PCl<sub>3</sub> gave MePCl<sub>2</sub>.AlCl<sub>3</sub>, which, treated with PhCH<sub>2</sub>CN gave MePCl<sub>2</sub> (I). Similarly Me<sub>2</sub>AlCl and PCl<sub>3</sub> gave [MePCl<sub>2</sub>]<sub>2</sub>AlCl<sub>3</sub>, which, treated with POCl<sub>3</sub> gave I. Methylaluminum sesquichloride and PCl<sub>3</sub> gave [MePCl<sub>2</sub>]<sub>3</sub>[Al<sub>2</sub>Cl<sub>6</sub>], which, treated with PhCH<sub>2</sub>CN gave I.

L4 ANSWER 57 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1975:410375 CAPLUS

DN 83:10375

OREF 83:1745a,1748a

TI Organometal complexes

IN Kroll, Wolfram R.; Long, Robert B.

PA Exxon Research and Engineering Co., USA  
SO U.S., 8 pp.  
CODEN: USXXAM  
DT Patent  
LA English  
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	-----	----	-----	-----	-----
PI	US 3868398	A	19750225	US 1970-65957	19700821 <--
PRAI	US 1970-65957	A	19700821		
AB	The complexation of CuCl with RAlCl <sub>2</sub> in an unsatd. solvent, Q, gave cuprous alkylchloroaluminates, CuAlRC <sub>13</sub> .2Q (R, Q given: Me, toluene; Et, cyclohexene; Me <sub>2</sub> CHCH <sub>2</sub> , cyclohexene; Me, 1-pentene). Ethylene was purged of ethane by use of CuAlEtCl <sub>3</sub> .2benzene and propylene was purged of propane by use of CuAlMeCl <sub>3</sub> in benzene.				

L4 ANSWER 58 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
AN 1974:121098 CAPLUS  
DN 80:121098  
OREF 80:19495a,19498a  
TI Dichloromethylphosphine  
IN Coates, Harold; Waring, Derek M. H.  
PA Minister of Supply, London  
SO Brit., 3 pp.  
CODEN: BRXXAA

DT Patent  
LA English

FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	-----	----	-----	-----	-----
PI	GB 1344051	A	19740116	GB 1951-18813	19510809 <--
	US 3840576	A	19741008	US 1952-303431	19520808 <--
PRAI	GB 1951-18813	A	19510809		
AB	MeAlCl <sub>2</sub> , Me <sub>2</sub> AlCl, or an equimol. mixture of the chlorides with PCl <sub>3</sub> gave complexes which with PhCH <sub>2</sub> CN or POC <sub>13</sub> gave MePCl <sub>2</sub> . Thus, 2.36 mole PCl <sub>3</sub> was treated with 325 g (2.36 mole) MeAlCl <sub>2</sub> in petroleum ether to give MePCl <sub>2</sub> .AlCl <sub>3</sub> . The complex (120 g) was added to 250 ml PhCH <sub>2</sub> CN at 20-5° to give 80% MePCl <sub>2</sub> .				

L4 ANSWER 59 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
AN 1971:141995 CAPLUS  
DN 74:141995  
OREF 74:22951a,22954a  
TI Complexes of plumbous chloride and dimethyllead dichloride with methylaluminum dichloride  
AU Boleslawski, M.; Pasynkiewicz, S.; Pszonka, H.  
CS Inst. Org. Chem. Technol., Tech. Univ., Warsaw, Pol.  
SO Journal of Organometallic Chemistry (1971), 28(3), C31-C33  
CODEN: JORCAI; ISSN: 0022-328X

DT Journal  
LA English

AB PbCl<sub>2</sub> and MeAlCl<sub>2</sub> formed the stable complex PbCl<sub>2</sub>.2AlMeCl<sub>2</sub>; treatment of the latter with PhCN gave PbCl<sub>2</sub> and 2PhCN.AlMeCl<sub>2</sub>. Me<sub>2</sub>PbCl<sub>2</sub> and MeAlCl<sub>2</sub> yielded the analogous Me<sub>2</sub>PbCl<sub>2</sub>.2AlMeCl<sub>2</sub>, which was associated in C<sub>6</sub>H<sub>6</sub>. The shift in the NMR signal of the Me group on the Al in these complexes, relative to free MeAlCl<sub>2</sub>, was comparable to that in 2PhCN.AlMeCl<sub>2</sub>.

L4 ANSWER 60 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
AN 1968:2989 CAPLUS  
DN 68:2989  
OREF 68:571a  
TI Methyl, aryl, and aralkyl derivs. from metals of Group II-V

IN Sundermeyer, Wolfgang; Verbeek, Wolfgang  
 PA Th. Goldschmidt AG  
 SO Ger., 5 pp.  
 CODEN: GWXXAW  
 DT Patent  
 LA German  
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 1239687 FR 1470956 GB 1132037 US 3480654	----	19670503   19691125	DE 1965-S95928 FR GB US	19650312 <--   19660311 <--
AB	<p>The title compds. can be prepared by treating the corresponding Me, aryl, or aralkyl halide with metal halides in molten nonoxidizing salt mixts. For this variation of the classical Wurtz synthesis, the metallic acceptor for halogen can be added to the mixture or can be obtained from the conducting salt by means of electrolysis. The second path yields the acceptor in a highly dispersed form. The metal halide formed during the reaction remains in solution. Thus, 270 g. Al is suspended in 2000 g. of a eutectic mixture from NaCl and AlCl<sub>3</sub>. MeCl (180 g.) is passed into the solution over 5 hrs. to yield 96% MeAlCl<sub>2</sub>, m. 73°. Similarly, 270 g. Al is suspended in 1919 g. of an equimolar mixture from NaCl and AlCl<sub>3</sub>. NaCl (292 g.) is added and at 220° 374 g. MeCl is added. Introduction of 170 g. MeSiCl<sub>3</sub> during 7 hrs. yields 91 g. SiMe<sub>4</sub>, b. 26°.</p> <p>Alternatively, 3000 g. of an equimolar mixture from NaCl and AlCl<sub>3</sub> are electrolyzed with 368.2 amp./hr. at 220° for 12 hrs. to give 125.5 g. Al and 447 g. Cl. MeCl (350 g.) is passed into the solution during 4 hrs. and 240 g. SiCl<sub>4</sub> vapor is blown into the solution over 8 hrs. to give 94.5 g. SiMe<sub>4</sub>. Me<sub>4</sub>Sn is obtained in 95% yield from 220 g. SnCl<sub>4</sub> at 200° using the same procedure; similarly, 99% Me<sub>3</sub>B is formed from 138 g. BCl<sub>3</sub> at 150°. Me<sub>4</sub>Ge is obtained in 97% yield from 218.5 g. GeCl<sub>4</sub> at 180° in 5 hrs. and 77.5 g. AsMe<sub>3</sub> from 580 g. AsCl<sub>3</sub> over 10 hrs. Addition of 420 g. of a dry equimolar mixture from ZnCl<sub>2</sub> and KCl after electrolysis and MeCl introduction yields, after a total 8 hrs. at 150°, 76.5% ZnMe<sub>2</sub>. By these methods are prepared HgMe<sub>2</sub>, Me<sub>2</sub>PbCl<sub>2</sub>.AlCl<sub>3</sub>, and Me<sub>2</sub>PbCl<sub>2</sub>.2AlCl<sub>3</sub>. Al amalgam from 2600 g. Hg and 300 g. Al is covered with 1500 g. molten NaCl. A mixture from 139 g. MeCl and 137 g. Me<sub>3</sub>SiH is stirred into the solution at 220° to give SiMe<sub>4</sub> in 75% yield. Under these conditions only 35% of the starting material reacted. Alternatively, 3.5 moles NaCl/KCl and 10 moles Al are stirred into a molten mixture from 35:15:15 mole % NaCl/KCl/AlCl<sub>3</sub>. The mixture is topped with 400 g. PhBr at 140°. Stirring for 10 hrs. yields Na(PhAlCl<sub>2</sub>Br). After evaporation of 10% excess PhBr under reduced pressure 125 g. Me<sub>3</sub>SiCl is passed into the solution with vigorous stirring to give 97% SiMe<sub>4</sub>. Alternatively, 97 g. Mg powder is treated in 2000 g. of an equimolar molten mixture from NaCl and AlCl<sub>3</sub> with 107 g. PhCl at 200°. Subsequently, 80 g. Me<sub>3</sub>SiCl are passed into the solution to yield 12 g. SiMe<sub>4</sub>, 4 g. Me<sub>3</sub>SiCl, 28 g. PhSiMe<sub>3</sub>, and 13 g. Ph<sub>2</sub>. Liquid Sn (1500 g.) is placed into 924 g. KCl and 4550 g. SnCl<sub>2</sub> and 210 g. MeCl passed into the solution at 300° to give 54.5% Me<sub>3</sub>SnCl, b. 163-5°. Sn (3800 g.) in a molten mixture from 822 g. LiCl and 938 g. KCl is electrolyzed at 400° until 90 g. Li are dissolved in the Sn. A Si cathode and a W anode are used. Subsequently, 100 g. MeCl and 100 g. MeSiCl<sub>3</sub> are passed into the solution to give 6 g. SiMe<sub>4</sub> and 22 g. Me<sub>3</sub>SiCl. If an equimolar mixture from PhCl and Me<sub>3</sub>SiCl is used, PhSiMe<sub>3</sub> is obtained in 25% yield. Similarly, 3400 g. Pb is added to a molten mixture from 1055 g. LiCl and 938 g. KCl. Electrolysis is carried out at 400° using Pb as cathode and W as anode. After 60 g. Li passed into the lead, 100 g. MeCl and 100 g. MeSiCl<sub>3</sub> are blown into the solution to give 7 g. SiMe<sub>4</sub> and 31 g. Me<sub>3</sub>SiCl. An equimolar mixture from PhCl and Me<sub>3</sub>SiCl yields 28% Me<sub>3</sub>SiPh. Al (54 g.) is suspended in 80 g. of an equimolar mixture from NaCl and</p>				

AlCl<sub>3</sub>, 152 g. MeCl passed into the solution at 220°, and 255 g. SiCl<sub>4</sub> added to the closed system over 2 hrs. The pressure rose to 30 atmospheric. After 10 hrs. 60% Me<sub>2</sub>SiCl<sub>2</sub>, 10% Me<sub>3</sub>SiCl, 10% MeSiCl<sub>3</sub> and 20% SiCl<sub>4</sub> are obtained. More Al and MeCl for the same quantity of SiCl<sub>4</sub> and longer reaction times increase the yield of Me<sub>2</sub>SiCl<sub>2</sub>. Al (54 g.) is suspended in 500 g. of an equimolar mixture from NaBr and AlBr<sub>3</sub> and 150 g. PhBr passed into the solution at 220° to give Na(PhAlBr<sub>3</sub>). Addition of 100 g. Me<sub>3</sub>SiBr gives 46 g. PhSiBr<sub>3</sub>. Sn(CH<sub>2</sub>Ph)<sub>4</sub>, m. 43°, (67 g.) is obtained when 130 g. PhCH<sub>2</sub>Cl is passed into a molten mixture from 924 g. KCl, 4550 g. SnCl<sub>2</sub>, and 1500 g. Sn at 300° over 5 hrs.

L4 ANSWER 61 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1967:473640 CAPLUS

DN 67:73640

OREF 67:13887a,13890a

TI Organometallic compounds. XLV. Complex formation and reactions of methylaluminum compounds with diglyme

AU Lehmkuhl, Herbert; Schaefer, Rolf

CS Max-Planck-Inst. Kohlenforsch., Muelheim-Ruhr, Fed. Rep. Ger.

SO Justus Liebig's Annalen der Chemie (1967), 705, 23-31

CODEN: JLACBF; ISSN: 0075-4617

DT Journal

LA German

OS CASREACT 67:73640

AB cf. preceding abstract Complexes were formed from 2,2'-dimethoxydiethyl ether with AlMe<sub>3</sub>, AlMe<sub>2</sub>Cl, and AlMeCl<sub>2</sub>. The 1:2-adducts were stable while the 1:1 and 1:3-complexes gave up excess component on heating in vacuo to form the 1:2-complexes. Disproportionation to Me-richer compds. was observed on heating the complexes of AlMe<sub>2</sub>Cl and AlMeCl<sub>2</sub>. Diglyme reacted with Al and AlEt<sub>3</sub> to evolve C<sub>2</sub>H<sub>4</sub>. With AlMe<sub>2</sub>H, MeOEt, diglycol mono-Me ether and CH<sub>4</sub> were formed.

L4 ANSWER 62 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1967:463561 CAPLUS

DN 67:63561

OREF 67:11915a,11918a

TI Nuclear magnetic resonance spectra of methyl aluminum chloride-donor complexes in the presence of a small excess of methyl aluminum chloride or donor

AU Wanders, A. C. M.; Konijnenberg, E.

CS Central Lab., Staatsmijnen/DSM, Geleen, Neth.

SO Tetrahedron Letters (1967), (22), 2081-7

CODEN: TELEAY; ISSN: 0040-4039

DT Journal

LA English

AB N.M.R. spectra (A, B, C) of 1.0M MeAlCl<sub>2</sub>.(Me<sub>2</sub>CH)<sub>2</sub>O and 1.0M AlCl<sub>3</sub>.(Me<sub>2</sub>CH)<sub>2</sub>O; of the same mixture and 0.025M (MeAlCl<sub>2</sub>)<sub>2</sub>; and of the same mixture and 0.05M (Me<sub>2</sub>CH)<sub>2</sub>O were recorded at 30° in C<sub>6</sub>H<sub>6</sub>. C showed the characteristic pattern of the iso-Pr<sub>2</sub>O group, whereas B showed a superposition of 2 iso-Pr<sub>2</sub>O signals with the chemical shift between the tertiary H septets equal to the proton-proton coupling constant (6.6 Hz.). A resembled B with broadened signals and a smaller separation between iso-Pr<sub>2</sub>O signals. A and B indicated a net exchange of iso-Pr<sub>2</sub>O mols. between the 2 complexes and comparison with C suggested the necessity for the presence of free iso-Pr<sub>2</sub>O mols. for the exchange reaction, on the assumption that the exchange of complexed and free iso-Pr<sub>2</sub>O mols. is faster than the direct exchange of ether mols. between the 2 complexes. The assumption was confirmed by the temperature dependence of I in which the isopropyl doublets

completely coalesce and the 2 septets broaden and move towards each other, so that at 50° the mean life of an ether mol. bonded to either of the Al compds. is between 0.03 and 0.08 sec. These and other results

(Swift, et al., CA 61: 10207a; Mole and Surtees, 61: 13326b) show that a variety of exchange mechanism must be taken into account.

L4 ANSWER 63 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1967:28882 CAPLUS

DN 66:28882

OREF 66:5515a,5518a

TI Organometallic compounds of aluminum, silicon, germanium, tin, or lead with methyl groups

IN Wartik, Thomas; Barnes, Robert Lee

PA Koppers Co., Inc.

SO U.S., 8 pp.

CODEN: USXXAM

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	-----	----	-----	-----	-----
PI	US 3288828		19661129	US	19630226 <--

AB The title compds. are useful as fuel additives, catalysts, and intermediates. E.g., 37.4 millimoles aluminum carbide (Al<sub>4</sub>C<sub>3</sub>) was placed in the furnace of a dry flow reactor under N, the furnace was heated to 300°, 69.5 millimoles HCl was passed through the furnace at a controlled flow rate under anhydrous oxygen-free conditions, the products were passed through first trap cooled to -78° and a second trap cooled to -196°, and the substances in the first trap were redistd. to yield MeAlCl<sub>2</sub> m. 72.5-3.7°. Group IVA metal halides could be methylated by treating Al<sub>4</sub>C<sub>3</sub> and HCl with the Group IVA metal halides. E.g., 3.6 moles HCl, 1 mole Al<sub>4</sub>C<sub>3</sub>, and 1.1 moles SiCl<sub>4</sub> was treated at 150-200° under anhydrous conditions to yield 44.2 g. MeI-2SiCl<sub>3</sub>-2 b. 57-62°.

L4 ANSWER 64 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1966:52207 CAPLUS

DN 64:52207

OREF 64:9768c-d

TI Tetraalkyllead process

IN Beaird, Francis M., Jr.; Kobetz, Paul

PA Ethyl Corp.

SO 4 pp.

DT Patent

LA Unavailable

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	-----	----	-----	-----	-----
PI	US 3226409		19651228	US 1963-318081	19631022 <--
PRAI	US		19631022		

AB In the process for preparing Me<sub>4</sub>Pb (CA 57, 16656c) from NaPb alloy and MeCl in an inert solvent in the presence of a catalyst, less difficulty in discharging the reaction mass from the reactor and from fuming of the remaining Al-containing compds. is encountered if the catalyst comprises a trialkylaluminum or alkylaluminum chloride and an alkyl ether polyethylene glycol alcoholate of Na, Li, K, Mg, Ca, or B. When NaPb alloy was treated with a 9-fold excess of MeCl under the usual conditions in the presence of 1.1 weight-% Et<sub>3</sub>Al and 1.27 weight-% EtO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>Na based of NaPb alloy, 93% Me<sub>4</sub>Pb was obtained. Cf. following abstract

L4 ANSWER 65 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1965:472177 CAPLUS

DN 63:72177

OREF 63:13316b-c

TI Tetramethyllead preparation using alkyl aluminum-amine catalyst systems



IN Beaird, Francis M., Jr.; Kobetz, Paul  
PA Ethyl Corp.  
SO 3 pp.  
DT Patent  
LA Unavailable  
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 3188334		19650608	US 1963-318075	19631022 <--
PRAI	US		19631022		

AB Me4Pb is prepared by the reaction of  $\text{MgCl}$  with an alkali metal Pb alloy in the presence of an alkylaluminum compound and using lower alkyl amines as adjuvants. E.g., when the basic procedure of U.S. 3,188,332 is modified to use only 0.46 weight-%  $\text{Me}_3\text{Al}_2\text{Cl}_3$  and 0.5 mole  $\text{Bu}_3\text{N}$  per g.-atom Al, a yield of 70.5%  $\text{Me}_4\text{Pb}$  was obtained although the catalyst level was only half the normal amount. The reaction mass did not smoke or fume when exposed to a gaseous atmospheric

L4 ANSWER 66 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
AN 1964:429924 CAPLUS  
DN 61:29924

OREF 61:5179b-e

TI Identification of bond types in aluminum and titanium compounds and complexes

AU Sakurada, Vutaka; Huggins, Maurice L.; Anderson, William R., Jr.

CS Inst., Menlo Park, CA

SO Journal of Physical Chemistry (1964), 68(7), 1934-43  
CODEN: JPCHAX; ISSN: 0022-3654

DT Journal

LA Unavailable

GI For diagram(s), see printed CA Issue.

AB The structures of Me Al chlorides and oxidized  $\text{AlMe}_3$ , and the homogeneous reactions of Al Me compds. with  $\text{TiCl}_4$  and with  $\text{TiCl}_3$  in tetrahydrofuran (THF) were studied, using n.m.r. (nuclear magnetic resonance) spectra, supplemented by x-ray, infrared, and magnetic susceptibility data. From systematic n.m.r. studies of Me Al chlorides,  $\text{Al}_2\text{Me}_3\text{Cl}_{6-n}$  ( $n = 2, 3, 4, 5$ , and 6), it is concluded that  $\text{Al}_2\text{Me}_3\text{Cl}_3$  has structure I, and that  $\text{Al}_2\text{Me}_5\text{Cl}$  consists of an equimolar mixture of III and IV. Structure II has, at most, only a transitory existence. Although rapid intermol. and intramol. exchange of Me are indicated in Me Al chlorides,  $\text{Al}_2\text{Me}_n\text{Cl}_{6-n}$  ( $n = 2, 3, 4, 5$ , and 6), there appears to be no rapid intermol. exchange of Me attached to Al and Me of methoxy groups, in hydrocarbon solns. containing  $\text{Al}_2\text{Me}_6$  and  $(\text{AlMe}_2\text{OMe})_3$ , at room temperature. In homogeneous solution in THF at room temperature,

$\text{AlMe}_3$  (or  $\text{AlMe}_2\text{Cl}$ ) reacts with  $\text{TiCl}_4$  to produce  $\text{AlMe}_2\text{Cl}$  (or  $\text{AlMeCl}_2$ ),  $\text{TiCl}_3$ , and  $\text{CH}_4$ . Reaction between  $\text{AlMe}_3$  or  $\text{AlMe}_2\text{Cl}$  and  $\text{TiCl}_3$  also proceeds homogeneously in THF. Magnetic susceptibilities of the reaction solns., confirmed by measurements of the chemical shifts in the n.m.r. spectra for the Me protons of Me Al compds., show that the valence state of Ti is still trivalent after these reactions. Evidence for the existence of  $\text{TiCl}_2\text{Me}$  was obtained, but no pos. evidence for a complex compound including the 2 different metal atoms, Al and Ti.

L4 ANSWER 67 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
AN 1963:403882 CAPLUS  
DN 59:3882

OREF 59:765c-e

TI Reaction of  $\alpha$ -olefins with soluble catalysts of the Ziegler type and the initiation mechanism of ethylene polymerization

AU Shilov, A. E.; Shilova, A. K.; Bobkov, B. N.

SO Vysokomolekulyarnye Soedineniya (1962), 4, 1688-95  
CODEN: VMSSDA; ISSN: 0042-9368

DT Journal  
 LA Unavailable  
 AB The hypothesis of the ionic mechanism of initiation of polymerization of  $\alpha$ -olefins by the dicyclopentadienyltitanium dichloride-Me<sub>2</sub>AlCl system was proved exptl. The spectrum of the system in C<sub>6</sub>H<sub>6</sub> showed the presence of the complex (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(Me)Cl-MeAlCl<sub>2</sub> (I). Reduction of I in the presence of an  $\alpha$ -olefin gave (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiCl<sub>2</sub>AlClR<sub>2</sub> (R = alkyl or halogen). By analyzing the gaseous products of I with C<sub>3</sub>H<sub>6</sub>, it was assumed that after introducing  $\alpha$ -olefin on the Ti-Me bond, the reaction proceeds according to the mechanism of intramol. disproportionation.  $2(C_5H_5)_2Ti(Me)Cl.Al(Me)Cl_2 + CH_2:CHR \rightarrow 2(C_5H_5)_2TiClAl(Me)Cl_2 + CH_4 + CH_2:C(Me)R$ . In the reaction of I with heptene, there was a linear dependence of [I]<sup>1/2</sup> on time. Over a wide range, the velocity constant was proportional to the concentration of heptene. Concns. of Me<sub>2</sub>AlCl with ratios of Al:Ti from 2:1 to 15:1 exerted little effect on velocity of Ti reduction. The velocity of reduction of the system in the presence of  $\alpha$ -heptene and the velocity of polymerization of C<sub>2</sub>H<sub>4</sub> were proportional to the increase in elec. conductivity during formation of I.

L4 ANSWER 68 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1963:400497 CAPLUS  
 DN 59:497  
 OREF 59:67d,68a-b  
 TI Coordination polymerization of olefins. Catalyst studies. I. The infrared spectroscopic investigation of the systems (CH<sub>3</sub>)<sub>3</sub>Al-TiCl<sub>4</sub> and (CH<sub>3</sub>)<sub>2</sub>Zn-TiCl<sub>4</sub>  
 AU Gray, A. P.; Callear, A. B.; Edgecombe, F. H. C.  
 CS Du Pont Ltd., Kingston  
 SO Canadian Journal of Chemistry (1963), 41, 1502-10  
 CODEN: CJCHAG; ISSN: 0008-4042  
 DT Journal  
 LA Unavailable  
 AB An infrared spectroscopic investigation of the reaction between TiCl<sub>4</sub> and Me<sub>3</sub>Al in the vapor phase was carried out at 6 different reactant ratios. The study defined the course of the initial reactions; demonstrated the importance of equilibrium among the products in this system as contrasted with Me<sub>2</sub>Zn-TiCl<sub>4</sub>; indicated the relative alkylating power of trimethyl, dimethylchloro, and methyldichloro aluminum toward TiCl<sub>4</sub> and MeTiCl<sub>3</sub>; and supported the view that the active catalyst site in such systems is the Ti-C bond in reduced titanium alkyls. A new mode of decomposition of MeTiCl<sub>3</sub> leading to active catalysts was found which can account for reported variable catalyst activities at Al/Ti ratios less than 1. Individual infrared spectra in the range 1500 to 300 cm.<sup>-1</sup> for Me<sub>3</sub>Al, Me<sub>2</sub>AlCl, MeAlCl<sub>2</sub>, MeTiCl<sub>3</sub>, and Me<sub>2</sub>TiCl<sub>2</sub>, as well as those of the initial reaction mixts., are presented.

L4 ANSWER 69 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1962:23081 CAPLUS  
 DN 56:23081  
 OREF 56:4347g-h  
 TI Alkyl aluminum halide complexes with alkali metal halides  
 AU Sleddon, G. J.  
 CS Imperial Chem. Inds., Ltd., Stevenston, UK  
 SO Chemistry & Industry (London, United Kingdom) (1961) 1492-3  
 CODEN: CHINAG; ISSN: 0009-3068  
 DT Journal  
 LA Unavailable  
 AB The complexes MRAIX<sub>3</sub>, M = Li, Na, or K; R = Me or Et; X = Cl or Br, were prepared by heating together the alkyl halide and MeAlX<sub>2</sub> or EtAlX<sub>2</sub> in an inert atmospheric. With Na and K halides 2 layers formed, with the complex in the

lower one. The complexes are white or gray solids, slightly soluble in hydrocarbon, stable at atmospheric pressure but disproportionating and dissociating at lower pressures. They react with air but do not ignite spontaneously; they react violently with H<sub>2</sub>O and lower alcs. M.ps. are: K(CH<sub>3</sub>)AlCl<sub>3</sub>, 150°; Na(CH<sub>3</sub>)AlCl<sub>3</sub>, 125°; Li(CH<sub>3</sub>)AlCl<sub>3</sub>, 74°; K(C<sub>2</sub>H<sub>5</sub>)AlCl<sub>3</sub>, 94°; Na(C<sub>2</sub>H<sub>5</sub>)AlCl<sub>3</sub>, 73°; Li(C<sub>2</sub>H<sub>5</sub>)AlCl<sub>3</sub>, 33°.

L4 ANSWER 70 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1961:48356 CAPLUS

DN 55:48356

OREF 55:9282e-g

TI Group IIb organometallic compounds

IN Blitzler, Sidney M.; Pearson, Tillmen H.

PA Ethyl Corp.

DT Patent

LA Unavailable

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 2969381		19610124	US 1959-810235	19590501 <--
AB	The title compds. are made by the reaction between the Zn, Cd, or Hg salts of organic acids and an organo B or Al compound. Thus, Et <sub>3</sub> B 3.9, Hg(OAc) <sub>2</sub> 6.4, and MeOCH <sub>2</sub> CH <sub>2</sub> OMe 70 is stirred under an inert atmospheric, refluxed 2 hrs., after cooling OH 5 in H <sub>2</sub> O 15 added, the heavy liquid phase at the bottom of the reactor withdrawn, and distilled to yield Et <sub>2</sub> Hg 3.4 parts. The following compds. are similarly made (compound, group IIb salt, B or Al compound, and diluent given): Et <sub>2</sub> Hg, Hg(OAc) <sub>2</sub> , Et <sub>3</sub> Al, MeOCH <sub>2</sub> CH <sub>2</sub> OMe; Et <sub>2</sub> Cd, Cd(OAc) <sub>2</sub> , Et <sub>3</sub> Al, Nujol; Et <sub>2</sub> Zn, Zn(OAc) <sub>2</sub> , Et <sub>3</sub> Al, Nujol; (n-C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> Hg, Hg(OPh) <sub>2</sub> , (n-C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> B, (MeOCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O; (CH <sub>2</sub> :CH) <sub>2</sub> Hg, (n-C <sub>7</sub> H <sub>15</sub> COO) <sub>2</sub> Hg, (CH <sub>2</sub> :CH) <sub>3</sub> B, Et <sub>3</sub> N; Et <sub>2</sub> Hg, Hg(OAc) <sub>2</sub> , NaBEt <sub>4</sub> , tetrahydrofuran. Higher yields, purer products, and faster reaction rates make this method superior to those based on alkyl halides or Grignard reagents.				

L4 ANSWER 71 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1960:33841 CAPLUS

DN 54:33841

OREF 54:6522i,6523a-d

TI Preparation and ignition properties of aluminum alkyls

AU Marsel, Charles J.; Kalil, Emil O.; Reidlinger, Anthony; Kramer, Leonard

CS New York Univ., New York, NY

SO Advances in Chem. Ser. (1959), 23, 172-83

DT Journal

LA Unavailable

AB To 4 lb. Al turnings in a 12 l. flask, connected to an efficient fractionating column, was added 2 lb. MeI, the whole refluxed until reaction was initiated, 23 lb. MeI added to keep pot temperature at 160° (external heating 24-48 hrs. usually necessary), and the whole distilled to give 50-65% Me<sub>3</sub>Al (I), b<sub>100</sub> 69-72°. Alternately, 320 g. Al foil, cut in small pieces, was treated 1st. with 5-6 ml. MeI, the reaction initiated by heat (temperature rise to 150°) the source of heat removed until the reaction subsided, MeCl introduced so that the internal pressure was equal to or greater than atmospheric pressure, and the temperature kept at 90-120° about 20 hrs. to give 100% mixture (II) of Me<sub>2</sub>AlCl and MeAlCl<sub>2</sub>. To 24 g. Na under N was added 100 g. II, the whole heated to initiate the reaction (95-100°), the exothermic reaction allowed to subside, and the mixture refluxed 5 hrs. to give 90% I. Al<sub>2</sub>Mg (60 g.) was treated 1st with a little MeI to initiate the reaction and then with MeCl for about 30 hrs. to give 80% Me<sub>2</sub>AlCl, b. 126-7°. I was unaffected when kept 2 hrs. at 300°F. in an autoclave, but about 30% decomposition

occurred after 6 hrs. at 450°F. and Et<sub>3</sub>Al was unchanged after 2 hrs. at 300°F. I was without effect in most metals but it attacked plastics (except Kel F and Teflon), silicon rubbers, synthetic and natural rubbers. When I was sprayed into air at 450°F., spontaneous ignition occurred after 0.013 sec. delay; a comparison of delay in ignition (sec.) under the same conditions for several other organometallic compds. was: Me<sub>2</sub>AlCl, 0.020; Et<sub>3</sub>Al, 0.040; Et<sub>2</sub>AlBr, 0.150; Et<sub>2</sub>Zn, smoke after 0.040; Et<sub>3</sub>B, 0.020 and (Me<sub>2</sub>CHCH<sub>2</sub>)<sub>3</sub>Al, smoke only. The effects of temperature and pressure on the ignition of I were as follows [temperature (F.), absolute press. (inches Hg), and ignition delay (msec.) given]: 455-60°, 2, 21; 450-60°, 5, 13; 445-60°, 30, 3; and 350-65°, 5, 15. The literature was reviewed. 12 references.

L4 ANSWER 72 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1959:44791 CAPLUS  
 DN 53:44791  
 OREF 53:7990b-c  
 TI Aluminum haloorganic compounds  
 PA Badische Anilin- & Soda-Fabrik Akt.-Ges.  
 DT Patent  
 LA Unavailable  
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	GB 804059		19581105	GB 1956-31572	19561017 <--
AB	R(R'O)AlX, R(ArO)AlX, and RAlX <sub>2</sub> , where R is an alkyl group, Ar an aryl group, and X a halogen, may be prepared by the reaction of Al or Al-Mg with AlX <sub>3</sub> and a dialkyl or alkyl aryl ether at 100-220°/to 100 atmospheric E.g., AlCl <sub>3</sub> 40, coarse Al powder 20, and Et <sub>2</sub> O 150 was heated 8 hrs. at 170° in an autoclave to yield Et(EtO)AlCl 96 parts, b1 85°.				

L4 ANSWER 73 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1958:92411 CAPLUS  
 DN 52:92411  
 OREF 52:16202d-e  
 TI Alkylaluminum dihalides  
 PA Esso Research and Engineering Co.  
 DT Patent  
 LA Unavailable  
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	GB 790822		19580219	GB 1956-20578	19560703 <--
AB	MeAlCl <sub>2</sub> (I) and EtAlCl <sub>2</sub> (II) are prepared in a one-step reaction. When MeCl is passed into 100 g. Al powder, 247 g. AlCl <sub>3</sub> , and 1 ml. MeI in a flask equipped with Dry Ice condensers, the temperature rises from 61° to 123°. Distillation of the product yields 300 g. I, b100 99-100°, m. 73°. Similarly from Al, AlCl <sub>3</sub> , EtI, and EtCl is prepared II, b50 105-15°, b0.2 36-46.5°. The AlCl <sub>3</sub> can be added incrementally. The products can be extracted from the mixture with n-C <sub>7</sub> H <sub>16</sub> .				

L4 ANSWER 74 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1958:92410 CAPLUS  
 DN 52:92410  
 OREF 52:16202c-d  
 TI Organic compounds of aluminum  
 IN Ziegler, Karl; Koster, Roland; Lehmkuhl, Herbert  
 DT Patent  
 LA Unavailable  
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI US 2844615 19580722 US 1953-379294 19530909 <--  
AB See Brit. 779,874 (C.A. 52, 2050d).

L4 ANSWER 75 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1957:1529 CAPLUS

DN 51:1529

OREF 51:257a-d

TI Organosilicon compounds. IX. Gas-phase methylation of chlorosilanes

AU Beranek, Ludvik; Bazant, Vladimir

CS Czech, Acad. Sci., Prague

SO Chemicke Listy pro Vedu a Prumysl (1956), 50, 1250-60

CODEN: CLPRAN; ISSN: 0366-6832

DT Journal

LA Unavailable

AB cf. C.A. 50, 14446f. A study of reaction conditions on the course of methylation in the presence of Al supports the reaction scheme suggested by Hurd (C.A. 40, 64977). Treatment of 82.9 g. Al shavings with 153.0 g. MeCl in a Mo glass tube at 345° gave 0.8 g. Me<sub>2</sub>AlCl, 137.5 g. MeAlCl<sub>2</sub>, 18.1 g. AlCl<sub>3</sub>, 18.8 g. CH<sub>4</sub>, 1.9 g. C<sub>2</sub>H<sub>6</sub>, 1.1 g. C<sub>2</sub>H<sub>4</sub>, 0.48 g. H, 0.33 g. HCl, and 46.3 g. C. With rising temperature the yields were lowered. Similarly methylated was MeSiCl<sub>3</sub> to Me<sub>2</sub>SiCl<sub>2</sub>, Me<sub>3</sub>SiCl, and Me<sub>4</sub>Si in amts. that varied according to the exptl. conditions. Addition of H brought about an increased conversion. Methylation of Et<sub>2</sub>SiCl<sub>2</sub> at 350° gave Me<sub>3</sub>SiCl (3.6), Me<sub>3</sub>SiEt (10.3), Me<sub>2</sub>EtSiCl (12.4), MeEt<sub>2</sub>SiCl (I) (10.9), and Et<sub>3</sub>SiCl (23.2%). Ph<sub>2</sub>SiCl<sub>2</sub> was methylated at 360°, the reaction product dissolved in dry Et<sub>2</sub>O, ethylated with EtMgCl, and hydrolyzed with 5% HCl to yield 50.7 g. C<sub>6</sub>H<sub>6</sub>, 13.3 g. PhMe, 20.5 g. MeEt<sub>2</sub>SiPh (II), 7.3 g. PhSiEt<sub>3</sub>, 4.4 g. MePh<sub>2</sub>SiEt, and 34.35 g. Ph<sub>2</sub>SiEt<sub>2</sub>, besides small amts. of Me<sub>2</sub>SiEt<sub>2</sub> and MeSiEt<sub>3</sub> and a polymerized thermoplastic residue, b. above 300°, containing 18.43% Si. II, b. 209.5-10.0°, d<sub>20</sub> 0.8886, n<sub>D</sub> 1.4975, was identified by heating 6.31 g. II to 70° for 10 min. with 8.5 mL. concentrated H<sub>2</sub>SO<sub>4</sub> and diluting the mixture with 43.5 mL.

H<sub>2</sub>O to

give 2.9 g. MeEt<sub>2</sub>SiOSiEt<sub>2</sub>Me (III), b. 188-90°, d<sub>20</sub> 0.8388, n<sub>D</sub> 1.4199. Treatment of 2.48 g. III dissolved in 4.2 mL. 98.6% H<sub>2</sub>SO<sub>4</sub> with 1.9 g. powdered NH<sub>4</sub>Cl under stirring and cooling yielded 1.58 g. I.

L4 ANSWER 76 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1956:20180 CAPLUS

DN 50:20180

OREF 50:4197a

TI Methylaluminum dichloride

IN Coates, Harold; Hunter, Wm. H.; Topley, Bryan

PA Minister of Supply

DT Patent

LA Unavailable

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	US 2712546		19550705	US 1952-308725	19520909 <--
AB	See Brit. 718,198 (C.A. 49, 14023f).				

L4 ANSWER 77 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1955:73613 CAPLUS

DN 49:73613

OREF 49:14023f-g

TI Methylaluminum dichloride

IN Coates, Harold; Hunter, Wm. H.; Topley, Bryan

PA Minister of Supply

DT Patent

LA Unavailable

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	GB 718198		19541110	GB 1951-29139	19511212 <--
AB	Me <sub>2</sub> AlCl (I) or mixed I and MeAlCl <sub>2</sub> (II) in C <sub>6</sub> H <sub>6</sub> treated slowly at 0° with Cl in C <sub>6</sub> H <sub>6</sub> with stirring is converted to II, recoverable by distillation, and the MeCl produced recycled. (Another way to manufacture II is to treat Al with Cl and MeCl.) Thus I 113 g. in C <sub>6</sub> H <sub>6</sub> 222 g. at 0° treated with Cl 87 g. in C <sub>6</sub> H <sub>6</sub> 300 cc. the C <sub>6</sub> H <sub>6</sub> distilled off after the reaction and the residue fractionated yielded 116 g. II. Cf. C.A. 46, 887d.				

L4 ANSWER 78 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1952:5274 CAPLUS

DN 46:5274

OREF 46:887d-i

TI Ketones from acyl chlorides and alkyl aluminum chlorides. A selective keto-ester synthesis

AU Adkins, Homer; Scanley, Clyde

CS Univ. of Wisconsin, Madison

SO Journal of the American Chemical Society (1951), 73, 2854-6

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA Unavailable

OS CASREACT 46:5274

AB p-NCC<sub>6</sub>H<sub>4</sub>Me with CrO<sub>3</sub> in AcOH-H<sub>2</sub>SO<sub>4</sub> yielded p-NCC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H (I), m. 218.5-19.3° (corrected). I refluxed 4 hrs. with 7 equivs. of SOCl<sub>2</sub> yielded the acid chloride (II). Convenient procedures are described for the preparation of MeAlCl<sub>2</sub> (III), Me<sub>2</sub>AlCl (IV), Me<sub>2</sub>AlCl.MeAlCl<sub>2</sub> (V), and EtAlCl<sub>2</sub> (VI). Attempts to prepare the Pr and Bu compds. were unsuccessful. With simple acid chlorides, RCOCl, only 0.6 mol. III is required for the preparation of the corresponding ketone, RCOMe, with a carbalkoxyacyl chloride, R'O<sub>2</sub>C(CH<sub>2</sub>)<sub>n</sub>COCl, an addnl. equivalent of III is required because it forms a complex with the ester: 1.1 mole III (35% in C<sub>6</sub>H<sub>6</sub>) added slowly under N (10-15°) to 0.5 mole ester acid chloride in 1-4 vols. C<sub>6</sub>H<sub>6</sub>, and the solution allowed to stand at room temperature 2 hrs., and then run into 500 g.

ice, or water below 30°, yielded the ketone (Table I). III (27.1 g. as 39% solution in C<sub>6</sub>H<sub>6</sub>) added at 45° during 12 min. to 12.2 g. in 150 cc. C<sub>6</sub>H<sub>6</sub>, the mixture allowed to stand 30 min. at 50°, hydrolyzed below 30°, and the C<sub>6</sub>H<sub>6</sub> layer distilled yielded 2.45 g. product, b<sub>15</sub> 210° (not investigated), and 11.9 g. p-cyanobenzophenone, m. 113.5-14.5° (from 60% EtOH); oxime, m. 171.5-4.5°. Table I, RCOCl, Semicarbazone,; R Albalide, R, Product, Yield (%), B. p./mm., n<sub>D</sub><sup>25</sup>, m.p.; III, Ph, BzMe, 81, 88-90°/17, 1.5323, 200-1°; V, Ph, BzEt, 89, 139-42°/79, 1.5253, 177.5-8.5°; III, Pr, PrAc, 70, 99-101°/740, -, 109.5-10.5°; IV, Pr, PrAc, 65, 99-101°/740, -, 109.5-10.5°; III, 9-phenanthryl, C<sub>14</sub>H<sub>9</sub>Ac, 78, 187°/1, -, oxime 152.5-3.5°; V, 9-phenanthryl, C<sub>14</sub>H<sub>9</sub>COEt, 86, 185°/1, -, 53.6-4.7° (free ketone); III, -(CH<sub>2</sub>)<sub>4</sub>-, Ac(CH<sub>2</sub>)<sub>4</sub>Ac, 35, 115°/13, -, 41-2.5° (free ketone) dioxime 148-51°; III, (CH<sub>2</sub>)<sub>8</sub>CO<sub>2</sub>Et, Ac(CH<sub>2</sub>)<sub>8</sub>CO<sub>2</sub>Et, 93, 118-23°/2, 1.4398, 112.5-13.6°; V, (CH<sub>2</sub>)<sub>8</sub>CO<sub>2</sub>Et, EtCO(CH<sub>2</sub>)<sub>8</sub>CO<sub>2</sub>Et, 94, 133-6°/2, 1.4411, 164.5-66° (free acid); III, (CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>Et, Ac(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>Et, 36, 103-4°/25, 1.4214, 100.5-1.5° (a); Bz(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>Et, 38, 125-7°/2, 1.5189, 116-18° (free acid); III, (CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>Me, Ac(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>Me, 24, 80.5-81°/12, -, 129.5-31.0° (oxime of free acid); III, (CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>Et, Ac(CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>Et, 92-5, 73°/1, 1.4304, -; V, (CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>Et, Ac(CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>Et, 90, 73°/1, 1.4308, -; VI, (CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>Et, EtCO(CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>Et, 94, 88-93°/2, 1.4329, 88-8.6°; (a)

2,4-Dinitrophenylhydrazone.

L4 ANSWER 79 OF 79 CAPLUS COPYRIGHT 2008 ACS on STN

AN 1940:21187 CAPLUS

DN 34:21187

OREF 34:3236a-i,3237a-b

TI Organoaluminum compounds. I. Methods of preparation

AU Grosse, Aristid V.; Mavity, Julian M.

SO Journal of Organic Chemistry (1940), 5, 106-21

CODEN: JOCEAH; ISSN: 0022-3263

DT Journal

LA Unavailable

AB After a review of the literature on organoaluminum compds. the various methods for their preparation, viz., the reaction of alkyl or aryl halides with Al (I), the reaction of 2 or more Al compds. with each other to produce another (II), and the use of other metals (III), are described and the possible number of compds. formed in these reactions is illustrated. Since organoaluminum compds. are decomposed by moisture and by O the reactions are carried out in an inert dry atmospheric. The aliphatic compds. are analyzed by measuring the hydrocarbons evolved on hydrolysis, the aromatic and some aliphatic by determination of the halogen or the Al as 8-hydroxyquinolate. In method I the reaction is carried out in an all-glass apparatus equipped with a stirrer and under cooling. EtCl and Al give a mixture of EtAlCl<sub>2</sub> (IV) and Et<sub>2</sub>AlCl (V) which when distilled, using a Podbielniak column, b<sub>20</sub> 120-2°, with IV concentrating in the lower-boiling fractions. MeCl and Al give a mixture of Me<sub>2</sub>AlCl (VI), b<sub>100</sub> 70-6°, b<sub>200</sub> 83-4°, and MeAlCl<sub>2</sub> (VII) which are separated by fractional distillation VII b<sub>100</sub> 97-101°, m. 72.7° after crystallization from C<sub>5</sub>H<sub>12</sub>. MeBr and Al give Me<sub>2</sub>AlBr, b<sub>50</sub> 74-7°, which crystallizes on cooling with dry ice, and MeAlBr<sub>2</sub>, b<sub>50</sub> 124-39°, m. 79° after crystallization from C<sub>5</sub>H<sub>12</sub>. Some disproportionation occurs during the distillation PrI and Al give a mixture of Pr<sub>2</sub>AlI (VIII) and PrAlI<sub>2</sub> (IX) which can be partially separated

into

6 fractions: (1) b<sub>1.0-0.8</sub> 80-128°, containing 77.4% VIII and 22.6% IX; (2) b<sub>0.8-0.7</sub> 128°, containing 62.9% VIII and 37.1% IX; (3) b<sub>0.7-0.5</sub> 128-7°; (4) b<sub>0.5-0.7</sub> 127-42°; (5) b<sub>0.7-0.5</sub> 142-3° containing 2.5% VIII and 97.5% IX; and (6) b<sub>0.5-0.4</sub> 143-39° containing 73.7% IX and 26.3% AlI<sub>3</sub>. The latter is due to disproportionation. The purest IX, crystallized from C<sub>5</sub>H<sub>12</sub>, m. 3-4°. MeI and Al give a mixture which on distillation at 50 mm. decomps. by disproportionation and gives

chiefly

Me<sub>2</sub>AlI, b<sub>50</sub> 109-10.5°, Me<sub>3</sub>Al and AlI<sub>3</sub>. EtBr and EtI readily react with Al but no satisfactory separation of the mono- and dialkyl compds. can be obtained. For the next Al derivs. method II is used. When an Et Al sesquichloride (X) distillate containing 21.17 g. V and 36.43 g. IV is heated with 22.8 g. AlCl<sub>3</sub> at 180-90° until a clear solution is obtained, 57.16 g. IV, b<sub>50</sub> 114.5-15.5°, m. 32°, is obtained. When to X containing 17.3 g. V and 26 g. IV, 23.09 g. Et<sub>3</sub>Al is added, the mixture becomes hot and on fractionation V, b<sub>50</sub> 125-6°, in 77% yield, is obtained. Et Al sesquibromide (XI) and AlBr<sub>3</sub> similarly give EtAlBr<sub>2</sub>, b<sub>10</sub> 120-2.5°, m. 23.5-4.4°. When 18.4 g. Me<sub>2</sub>AlI and 38.5 g. AlI<sub>3</sub> are melted together at 170° and distilled at 0.2 mm., strong disproportionation takes place and 11.9 g. MeAlI<sub>2</sub>, m. 68-71°, is obtained. Distillation of a mixture of 10 g. Et<sub>3</sub>Al and 17.5 g. AlI<sub>3</sub> gives

Et<sub>2</sub>AlI.

On vacuum fractionation of Et Al sesquiodide disproportionation occurs and fractions containing 97-8% EtAlI<sub>2</sub> and 2-3% Et<sub>2</sub>AlI are obtained from which on repeated crystallization from C<sub>5</sub>H<sub>12</sub>, EtAlI<sub>2</sub>, m. 39-40°, can be isolated. When a mixture of 6.63 g. Ph<sub>3</sub>Al and 6.92 g. AlCl<sub>3</sub> is heated for 20 min. at 200° and then distilled in vacuo, a fraction (2.79 g.) b<sub>7-15</sub> 103-77°, and a fraction (7.87 g.) b<sub>15-0.5</sub> 177-208° are obtained. The latter, PhAlCl<sub>2</sub>, recrystd. from C<sub>6</sub>H<sub>6</sub>, m. 93-5.5°.

Sublimation gives white needles, m. 94-5°. In a similar way PhAlBr<sub>2</sub>, m. 73.5-8°, is obtained. PhAlI<sub>2</sub> is prepared from Ph Al sesquiodide and AlI<sub>3</sub> by heating the mixture for 0.5 hr. at 100° until it becomes completely liquid. It is dissolved in C<sub>6</sub>H<sub>6</sub>, filtered and concentrated. On standing, PhAlI<sub>2</sub> crystallizes in white prisms, m. 106-10°. p-MeC<sub>6</sub>H<sub>4</sub>AlI<sub>2</sub> prepared in a similar way m. 140-5°. When 5.8 g. Al(OMe)<sub>3</sub> and 6.95 g. Me<sub>3</sub>Al are gradually mixed, considerable heat is evolved. The mixture is heated for 20 min. at 100° and finally at 135°. On distillation the fraction b<sub>10</sub> 87-8° consists of Me<sub>2</sub>AlOMe, m. 30-3°. MeAl(OMe)<sub>2</sub> is prepared by mixing 6.5 g. Me<sub>3</sub>Al and 21.7 g. Al(OMe)<sub>3</sub> and heating the mixture at 280°. On heating a mixture of 3.34 g. Al(OEt)<sub>3</sub> and 4.5 g. AlEt<sub>3</sub> at 170° and distillation, Et<sub>2</sub>AlOEt, b<sub>10</sub> 108-9°, m. 2.5-4.5°, is obtained. EtAl(OEt)<sub>2</sub>, b<sub>1</sub> 137°, is prepared in a similar way from 15.24 g. Al(OEt)<sub>3</sub> and 5.62 g. AlEt<sub>3</sub>. By method III, the following Al derivs. are prepared: Et<sub>2</sub>AlBr (XII) is prepared by gradual addition of 496 g. EtBr to 107 g. magnalium turnings (30% Mg, 70% Al) with I as catalyst. The mixture is then heated for 1 hr. at 120-40° and distilled XII b<sub>2</sub> 75°; the yield is 91%. When 150 g. XII is added to 50.3 g. Na ribbon and the mixture heated to 105°, a vigorous reaction sets in. After this has ceased 186 g. more XII is added, it is then heated first for 1 hr. at 110°, then for 16 hrs. at 200-10° and distilled at 2 mm. The distillate (107.4 g.) is retreated with Na and finally fractionated through a Podbielniak column. AlEt<sub>3</sub> b<sub>50</sub> 128-30°. When XI is treated with Na, XII, b<sub>50</sub> 147-8°, is formed. Treatment of Me Al sesquichloride and Na, followed by a treatment with Na-K (23% K) gives AlMe<sub>3</sub>, b<sub>755</sub> 125-6°, in 63% yield. It crystallizes on cooling. PrI and magnalium give VIII, b<sub>4.2-4.7</sub> 153-6°, in 66% yield.

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DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE	TOTAL
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